

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 636 164 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
24.05.2000 Bulletin 2000/21

(51) Int. Cl.⁷: **C10L 1/18**, C07C 69/76,
C08G 65/32

(21) Application number: **94904495.2**

(86) International application number:
PCT/US93/12361

(22) Date of filing: **17.12.1993**

(87) International publication number:
WO 94/14926 (07.07.1994 Gazette 1994/15)

**(54) POLY(OXYALKYLENE) HYDROXYAROMATIC ESTERS AND FUEL COMPOSITIONS
CONTAINING THE SAME**

POLY(OXYALKYLEN)HYDROXYAROMATISCHE ESTER UND DIESE ENTHALTENDE
BRENNSTOFFZUSAMMENSETZUNGEN

ESTERS POLY(OXYALKYLENE) HYDROXYAROMATIQUES ET COMPOSITIONS COMBUSTIBLES
LES CONTENANT

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE**

(72) Inventor: **CHERPECK, Richard, E.**
Cotati, CA 94931 (US)

(30) Priority: **18.12.1992 US 993179**

(74) Representative:
Nash, David Allan et al
Haseltine Lake & Co.,
Imperial House, 15-19 Kingsway
London WC2B 6UD (GB)

(43) Date of publication of application:
01.02.1995 Bulletin 1995/05

(73) Proprietor:
Chevron Chemical Company LLC
San Francisco, CA 94105 (US)

(56) References cited:
WO-A-94/14925 **US-A- 2 937 933**
US-A- 3 758 282 **US-A- 3 944 594**
US-A- 4 032 562 **US-A- 4 245 030**
US-A- 4 430 093 **US-A- 5 296 003**

EP 0 636 164 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**BACKGROUND OF THE INVENTION**5 Field of the Invention

[0001] This invention relates to poly(oxyalkylene) hydroxyaromatic esters and their use in fuel compositions to prevent and control engine deposits.

10 Description of the Related Art

[0002] It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports and intake valves, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

[0003] For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Kreuz et al., discloses a motor fuel composition comprising a mixture of hydrocarbons in the gasoline boiling range containing about 0.01 to 0.25 volume percent of a high molecular weight aliphatic hydrocarbon-substituted phenol in which the aliphatic hydrocarbon radical has an average molecular weight in the range of about 500 to 3,500. This patent teaches that gasoline compositions containing minor amount of an aliphatic hydrocarbon-substituted phenol not only prevent or inhibit the formation of intake valve and port deposits in a gasoline engine, but also enhance the performance of the fuel composition in engines designed to operate at higher operating temperatures with a minimum of decomposition and deposit formation in the manifold of the engine.

[0004] Similarly, U.S. Patent No. 4,134,846, issued January 16, 1979 to Machleder et al., discloses a fuel additive composition comprising a mixture of (1) the reaction product of an aliphatic hydrocarbon-substituted phenol, epichlorohydrin and a primary or secondary mono- or polyamine, and (2) a polyalkylene phenol. This patent teaches that such compositions show excellent carburetor, induction system and combustion chamber detergency and, in addition, provide effective rust inhibition when used in hydrocarbon fuels at low concentrations.

[0005] Fuel additives containing a poly(oxyalkylene) moiety are also known in the art. For example, U.S. Patent No. 4,191,537, issued March 4, 1980 to R. A. Lewis et al., discloses a fuel composition comprising a major portion of hydrocarbons boiling in the gasoline range and from 30 to 2000 ppm of a hydrocarbyl poly(oxyalkylene) aminocarbamate having a molecular weight from about 600 to 10,000, and at least one basic nitrogen atom. The hydrocarbyl poly(oxyalkylene) moiety is composed of oxyalkylene units selected from 2 to 5 carbon oxyalkylene units. These fuel compositions are taught to maintain the cleanliness of intake systems without contributing to combustion chamber deposits.

[0006] Aromatic compounds containing a poly(oxyalkylene) moiety are also known in the art. For example, the above-mentioned U.S. Patent No. 4,191,537, discloses alkylphenyl poly(oxyalkylene) polymers which are useful as intermediates in the preparation of alkylphenyl poly(oxyalkylene) aminocarbamates.

[0007] Additionally, hydroxyaromatic compounds containing a poly(oxyalkylene) moiety are known in the art. For example, U.S. Patent No. 4,952,732, issued August 28, 1990 to G. P. Speranza et al., discloses Mannich condensates prepared from a phenol, formaldehyde and an alkylamine containing propoxy groups and, optionally, ethoxy groups. These Mannich condensates are taught to be useful as corrosion inhibitors, water repellent agents, paint adhesion promoters, and also as intermediates for preparing surfactants, and pololys finding use in the manufacture of polyurethane foam.

[0008] US-4032562 relates to esters of polyalkyleneglycols with 3,5-dialkyl-4-hydroxyphenylalkanoic acids and teaches that these compounds are useful as stabilisers of organic substrates subject to oxidative and thermal degradation.

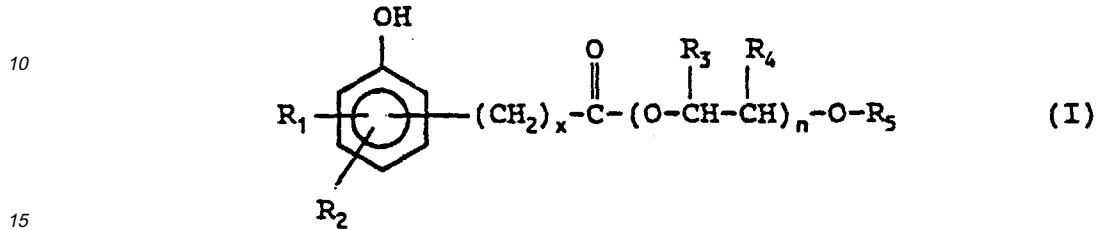
[0009] US-3944594 relates to hindered phenolic esters of oligomeric glycols and thioglycols and teaches that these compounds may be useful as stabilisers of organic materials normally subject to oxidative deterioration.

[0010] It has now been discovered that certain hydroxyaromatic esters having a poly(oxyalkylene) "tail" provide excellent control of engine deposits, especially intake valve deposits, when employed as fuel additives in fuel compositions. Moreover, these poly(oxyalkylene) hydroxyaromatic esters have been found to produce fewer combustion chamber deposits than known aliphatic hydrocarbon-substituted phenolic fuel additives.

SUMMARY OF THE INVENTION

[0011] The present invention provides novel poly(oxyalkylene) hydroxyaromatic esters which are useful as fuel additives for the prevention and control of engine deposits, particularly intake valve deposits.

5 **[0012]** The first aspect of the present invention relates to the use of poly(oxyalkylene) hydroxyaromatic esters having the formula:

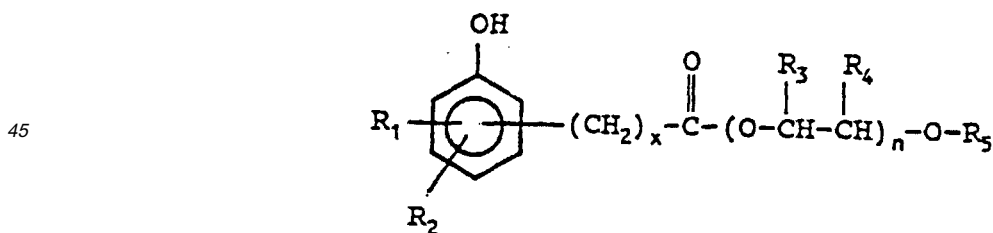


or a fuel-soluble salt thereof; wherein R_1 and R_2 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R_3 and R_4 are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R_5 is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:



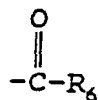
wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; R_7 and R_8 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; n is an integer from 5 to 100; and x and y are each independently an integer from 0 to 10; as an additive in a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range, for the control of engine deposits.

[0013] The second aspect of the present invention relates to poly(oxyalkylene) hydroxyaromatic esters having the formula:



or a fuel-soluble salt thereof; wherein R_1 and R_2 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R_3 and R_4 are each hydrogen or ethyl, wherein one of R_3 and R_4 is ethyl and the other is hydrogen; R_5 is hydrogen, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:

55

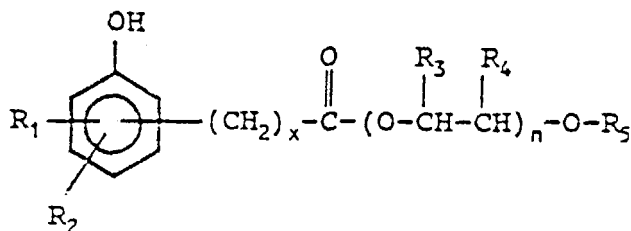


5

wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; n is an integer from 10 to 50; and x is an integer from 0 to 10.

10 **[0014]** The present invention further provides a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an effective deposit-controlling amount of a hydroxyaromatic poly(oxyalkylene) ester having the formula:

15



20

25 or a fuel-soluble salt thereof; wherein R₁ and R₂ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R₃ and R₄ are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R₅ is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:

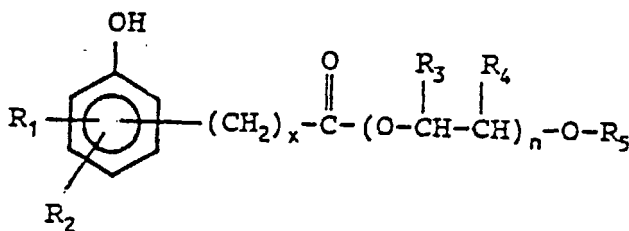
30



35 wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; n is an integer from 10 to 50; and x is an integer from 0 to 10.

[0015] The present invention additionally provides a fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 66°C to 200°C (150°F to 400°F) and from about 10 to 70 weight percent of a hydroxyaromatic poly(oxyalkylene) ester having the formula:

40



45

50

or a fuel-soluble salt thereof; wherein R₁ and R₂ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R₃ and R₄ are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R₅ is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:

55



5

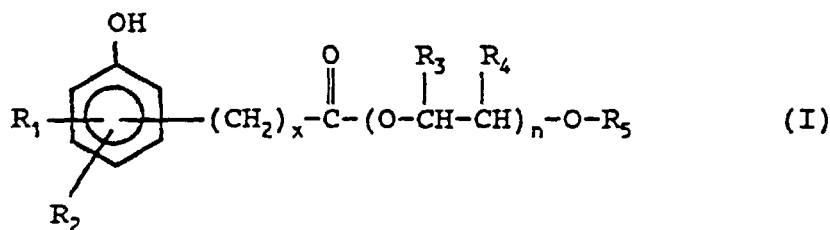
wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; n is an integer from 10 to 50; and x is an integer from 0 to 10.

10 **[0016]** Among other factors, the present invention is based on the surprising discovery that certain poly(oxyalkylene) hydroxyaromatic esters, when employed as fuel additives in fuel compositions, provide excellent control of engine deposits, especially on intake valves, and produce fewer combustion chamber deposits than known aliphatic hydrocarbon-substituted phenolic fuel additives.

15 DETAILED DESCRIPTION OF THE INVENTION

[0017] The compounds whose use in fuel additives is provided by the first aspect of the present invention have the general formula:

20



25

30 or a fuel-soluble salt thereof.

[0018] In this use aspect of the invention, preferably R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms. More preferably, R_1 is hydrogen or hydroxy. Most preferably, R_1 is hydrogen.

[0019] In this use aspect, R_2 is preferably hydrogen.

35 **[0020]** In this use aspect, preferably one of R_3 and R_4 is lower alkyl having 1 to 3 carbon atoms and the other is hydrogen. More preferably, one of R_3 and R_4 is methyl or ethyl and the other is hydrogen. Most preferably, one of R_3 and R_4 is ethyl and the other is hydrogen.

40 **[0021]** In this use aspect, R_5 preferably hydrogen, alkyl having 2 to 22 carbon atoms, or alkylphenyl having an alkyl group containing 2 to 24 carbon atoms. More preferably, R_5 is hydrogen, alkyl having 4 to 12 carbon atoms or alkylphenyl having an alkyl group containing 4 to 12 carbon atoms. Most preferably, R_5 is alkylphenyl having an alkyl group containing 4 to 12 carbon atoms.

[0022] In this use aspect, R_6 is preferably alkyl having 4 to 12 carbon atoms.

[0023] In this use aspect, preferably R_7 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms. More preferably, R_7 is hydrogen or hydroxy. Most preferably, R_7 is hydrogen.

[0024] In this use aspect R_8 is preferably hydrogen.

45 **[0025]** In this use aspect, preferably n is an integer from 10 to 50. More preferably, n is an integer from 15 to 30. Preferably, x is an integer from 0 to 2. More preferably, x is 0. Preferably, y is an integer from 0 to 2. More preferably, y is 0.

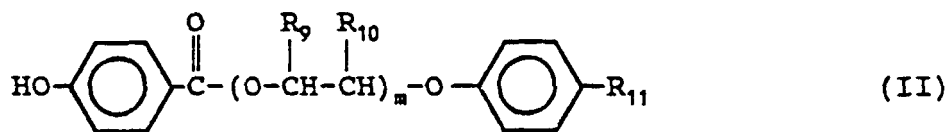
50 **[0026]** A preferred group of poly(oxyalkylene) hydroxyaromatic esters for use in accordance with this aspect of the present invention are those of formula I wherein R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is hydrogen; one of R_3 and R_4 is hydrogen and the other is methyl or ethyl; R_5 is hydrogen, alkyl having 2 to about 22 carbon atoms or alkylphenyl having an alkyl group containing 4 to about 24 carbon atoms; n is 15 to 30 and x is 0.

55 **[0027]** Another preferred group of poly(oxyalkylene) hydroxyaromatic esters for use in accordance with this aspect of the present invention are those of formula I wherein R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is hydrogen; one of R_3 and R_4 is hydrogen and the other is methyl or ethyl; R_5 is hydrogen, alkyl having 2 to about 22 carbon atoms or alkylphenyl having an alkyl group containing 4 to about 24 carbon atoms; n is 15 to 30 and x is 1 or 2.

[0028] A more preferred group of poly(oxyalkylene) hydroxyaromatic esters for use in accordance with this aspect of the present invention are those of formula I wherein R_1 is hydrogen or hydroxy; R_2 is hydrogen; one of R_3 and R_4 is

hydrogen and the other is methyl or ethyl; R_5 is hydrogen, alkyl having 4 to 12 carbon atoms or alkylphenyl having an alkyl group containing 4 to 12 carbon atoms; n is 15 to 30; and x is 0.

[0029] A particularly preferred group of poly(oxyalkylene) hydroxyaromatic esters for use in accordance with this aspect of the invention are those having the formula:



wherein one of R_9 and R_{10} is methyl or ethyl and the other is hydrogen; R_{11} is an alkyl group having 4 to 12 carbon atoms; and m is an integer from 15 to 30.

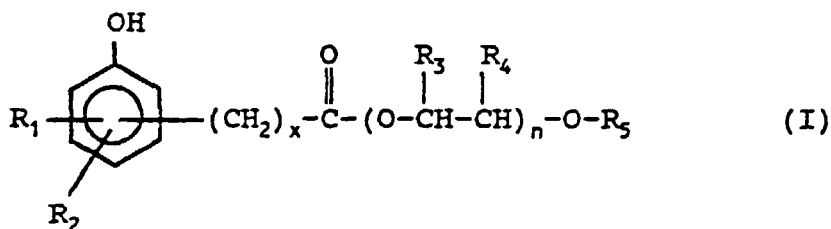
[0030] It is especially preferred that the aromatic hydroxyl group or groups present in the poly(oxyalkylene) hydroxyaromatic esters used in this aspect of the invention be situated in a *meta* or *para* position relative to the poly(oxyalkylene) ester moiety. When the aromatic moiety contains one hydroxyl group, it is particularly preferred that this hydroxyl group be in a *para* position relative to the poly(oxyalkylene) ester moiety.

[0031] The poly(oxyalkylene) hydroxyaromatic esters for use in accordance with this aspect of the present invention will generally have a sufficient molecular weight so as to be non-volatile at normal engine intake valve operating temperatures (about 200-250°C). Typically, the molecular weight of the poly(oxyalkylene) hydroxyaromatic esters for use in accordance with this aspect of the invention will range from about 600 to about 10,000, preferably from 1,000 to 3,000.

[0032] Generally, the poly(oxyalkylene) hydroxyaromatic esters for use in accordance with this aspect of the invention will contain an average of about 5 to about 100 oxyalkylene units; preferably, 10 to 50 oxyalkylene units; more preferably, 15 to 30 oxyalkylene units.

[0033] Fuel-soluble salts of the poly(oxyalkylene) hydroxyaromatic esters whose use is contemplated in this aspect of the present invention are also contemplated to be useful for preventing or controlling deposits. Such salts include alkali metal, alkaline earth metal, ammonium, substituted ammonium and sulfonium salts. Preferred metal salts are the alkali metal salts, particularly the sodium and potassium salts, and the substituted ammonium salts, particularly tetraalkyl-substituted ammonium salts, such as the tetrabutylammonium salts.

[0034] According to the second aspect of the present invention, there is provided compounds having the general formula:



or a fuel-soluble salt thereof.

[0035] In this compound aspect of the invention, preferably R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms. More preferably, R_1 is hydrogen or hydroxy. Most preferably, R_1 is hydrogen.

[0036] In this compound aspect of the invention, R_2 is preferably hydrogen.

[0037] In this compound aspect, one of R_3 and R_4 is ethyl and the other is hydrogen.

[0038] In this compound aspect, R_5 is preferably hydrogen, or alkylphenyl having an alkyl group containing 2 to 24 carbon atoms. More preferably, R_5 is hydrogen or alkylphenyl having an alkyl group containing 4 to 12 carbon atoms. Most preferably, R_5 is alkylphenyl having an alkyl group containing 4 to 12 carbon atoms.

[0039] In this compound aspect, R_6 is preferably alkyl having 4 to 12 carbon atoms.

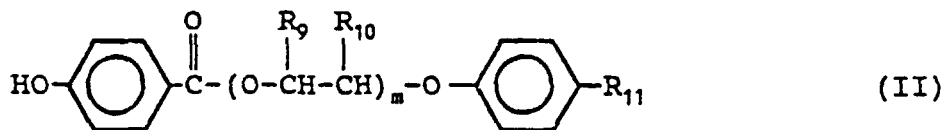
[0040] In this compound aspect, n is an integer from 10 to 50. More preferably, n is an integer from 15 to 30. Preferably, x is an integer from 0 to 2. More preferably, x is 0.

[0041] A preferred group of poly(oxyalkylene) hydroxyaromatic esters are those of formula I wherein R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is hydrogen; R_5 is hydrogen; n is 15 to 30 and x is 0.

[0042] Another preferred group of poly(oxyalkylene) hydroxyaromatic esters are those of formula I wherein R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is hydrogen; n is 15 to 30 and x is 1 or 2.

[0043] A more preferred group of poly(oxyalkylene) hydroxyaromatic esters are those of formula I wherein R_1 is hydrogen or hydroxy; R_2 is hydrogen; R_5 is hydrogen, n is 15 to 30; and x is 0.

[0044] A particularly preferred group of poly(oxyalkylene) hydroxyaromatic esters are those having the formula:



wherein one of R_9 and R_{10} is methyl or ethyl and the other is hydrogen; R_{11} is an alkyl group having 4 to 12 carbon atoms; and m is an integer from 15 to 30.

[0045] It is especially preferred that the aromatic hydroxyl group or groups present in the poly(oxyalkylene) hydroxyaromatic esters of this aspect of the invention be situated in a *meta* or *para* position relative to the poly(oxyalkylene) ester moiety. When the aromatic moiety contains one hydroxyl group, it is particularly preferred that this hydroxyl group be in a *para* position relative to the poly(oxyalkylene) ester moiety.

[0046] The poly(oxyalkylene) hydroxyaromatic esters of this aspect of the present invention will generally have a sufficient molecular weight so as to be non-volatile at normal engine intake valve operating temperatures (about 200-250°C). Typically, the molecular weight of the poly(oxyalkylene) hydroxyaromatic esters of this aspect of the invention will range from about 600 to about 10,000, preferably from 1,000 to 3,000.

[0047] Generally, the poly(oxyalkylene) hydroxyaromatic esters of this aspect of the invention will contain an average of about 5 to about 100 oxyalkylene units; preferably, 10 to 50 oxyalkylene units; more preferably, 15 to 30 oxyalkylene units.

[0048] Fuel-soluble salts of the poly(oxyalkylene) hydroxyaromatic esters of this aspect of the present invention are also contemplated to be useful for preventing or controlling deposits. Such salts include alkali metal, alkaline earth metal, ammonium, substituted ammonium and sulfonium salts. Preferred metal salts are the alkali metal salts, particularly the sodium and potassium salts, and the substituted ammonium salts, particularly tetraalkyl-substituted ammonium salts, such as the tetrabutylammonium salts.

Definitions

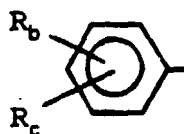
[0049] As used herein the following terms have the following meanings unless expressly stated to the contrary.

[0050] The term "alkyl" refers to both straight- and branched-chain alkyl groups.

[0051] The term "lower alkyl" refers to alkyl groups having 1 to about 6 carbon atoms and includes primary, secondary and tertiary alkyl groups. Typical lower alkyl groups include, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

[0052] The term "lower alkoxy" refers to the group $-OR_a$ wherein R_a is lower alkyl. Typical lower alkoxy groups include methoxy, ethoxy, and the like.

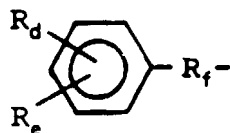
[0053] The term "alkaryl" refers to the group:



wherein R_b and R_c are each independently hydrogen or an alkyl group, with the proviso that both R_b and R_c are not hydrogen. Typical alkaryl groups include, for example, tolyl, xylyl, cumenyl, ethylphenyl, butylphenyl, dibutylphenyl, hexylphenyl, octylphenyl, dioctylphenyl, nonylphenyl, decylphenyl, didecylphenyl, dodecylphenyl, hexadecylphenyl, octadecylphenyl, icosylphenyl, tricontylphenyl and the like. The term "alkylphenyl" refers to an alkaryl group of the above formula in which R_b is alkyl and R_c is hydrogen.

[0054] The term "aralkyl" refers to the group:

5

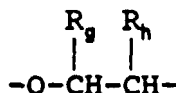


10

wherein R_d and R_e are each independently hydrogen or an alkyl group; and R_f is an alkylene group. Typical alkaryl groups include, for example, benzyl, methylbenzyl, dimethylbenzyl, phenethyl, and the like.

[0055] The term "oxyalkylene unit" refers to an ether moiety having the general formula:

15

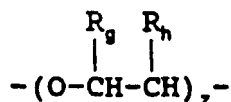


20

wherein R_g and R_h are each independently hydrogen or lower alkyl groups.

[0056] The term "poly(oxyalkylene)" refers to a polymer or oligomer having the general formula:

25



30

wherein R_g and R_h are as defined above, and z is an integer greater than 1. When referring herein to the number of poly(oxyalkylene) units in a particular poly(oxyalkylene) compound, it is to be understood that this number refers to the average number of poly(oxyalkylene) units in such compounds unless expressly stated to the contrary.

General Synthetic Procedures

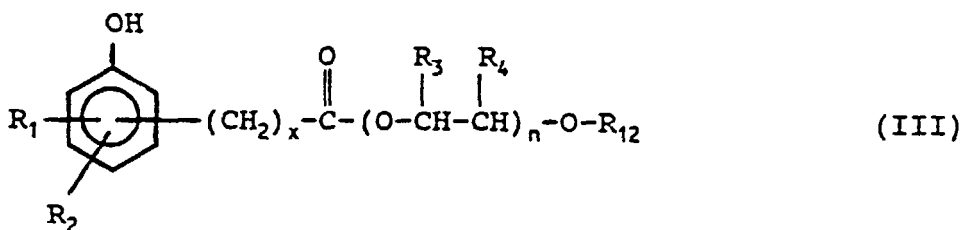
35

[0057] The poly(oxyalkylene) hydroxyaromatic esters of this invention and for use in this invention may be prepared by the following general methods and procedures. It should be appreciated that where typical or preferred process conditions (e.g. reaction temperatures, times, mole ratios of reactants, solvents, pressures, etc.) are given, other process conditions may also be used unless otherwise stated. Optimum reaction conditions may vary with the particular reactants or solvents used, but such conditions can be determined by one skilled in the art by routine optimization procedures.

40

[0058] The poly(oxyalkylene) hydroxyaromatic esters of the present invention or for use in the present invention having the formula:

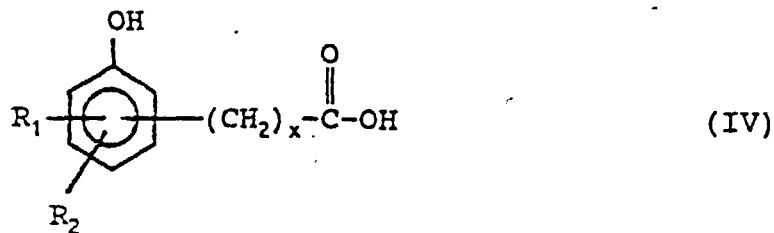
45



50

55

wherein R₁-R₄, n and x are as defined above and R₁₂ is an alkyl, phenyl, aralkyl or alkaryl group, may be prepared by esterifying a hydroxyaromatic carboxylic acid having the formula:



10 wherein R_1 , R_2 , and x are as defined above, with a poly(oxyalkylene) alcohol having the formula:



20 wherein R_3 , R_4 , R_{12} and n are as defined above, using conventional esterification reaction conditions.

[0059] The hydroxyaromatic carboxylic acids of formula IV are either known compounds or can be prepared from known compounds by conventional procedures. Suitable hydroxyaromatic carboxylic acids for use as starting materials in this invention are 2-hydroxybenzoic acid, 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,4,5-trihydroxybenzoic acid, 3-hydroxy-4-methoxybenzoic acid, 4-hydroxy-3-methoxybenzoic acid, 3-t-butyl-4-hydroxybenzoic acid, 3,5-di-t-butyl-4-hydroxybenzoic acid, 4-hydroxyacetic acid, 3-(4-hydroxyphenyl)propionic acid and the like.

[0060] The poly(oxyalkylene) alcohols of formula V may also be prepared by conventional procedures known in the art. Such procedures are taught, for example, in U.S. Patent Nos. 2,782,240 and 2,841,479, which are incorporated herein by reference.

[0061] Preferably, the poly(oxyalkylene) alcohols of formula V are prepared by contacting an alkoxide or phenoxide metal salt having the formula:



wherein R_{12} is as defined above and M is a metal cation, such as lithium, sodium, or potassium, with about 5 to about 100 molar equivalents of an alkylene oxide (an epoxide) having the formula:



45 wherein R_3 and R_4 are as defined above.

[0062] Generally, metal salt VI is prepared by contacting the corresponding hydroxy compound $R_{12}\text{OH}$ with a strong base, such as sodium hydride, potassium hydride, sodium amide and the like, in an inert solvent, such as toluene, xylene and the like, under substantially anhydrous conditions at a temperature in the range from about -10°C to about 120°C for about 0.25 to about 3 hours.

[0063] Metal salt VI is generally not isolated, but is reacted *in situ* with the alkylene oxide VII to provide, after neutralization, the poly(oxyalkylene) alcohol V. This polymerization reaction is typically conducted in a substantially anhydrous inert solvent at a temperature of about 30°C to about 150°C for about 2 to about 120 hours. Suitable solvents for this reaction, include toluene, xylene and the like. The reaction will generally be conducted at a pressure sufficient to contain the reactants and the solvent, preferably at atmospheric or ambient pressure.

[0064] The amount of alkylene oxide employed in this reaction will depend on the number of oxyalkylene units desired in the product. Typically, the molar ratio of alkylene oxide VII to metal salt VI will range from about 5:1 to about 100:1; preferably, from 10:1 to 50:1, more preferably from 15:1 to 30:1.

[0065] Suitable alkylene oxides for use in the polymerization reaction include, for example, ethylene oxide; propylene oxide; butylene oxides, such as 1,2-butylene oxide (1,2-epoxybutane) and 2,3-butylene oxide (2,3-epoxybutane); pentylene oxides; hexylene oxides; octylene oxides and the like. Preferred alkylene oxides are propylene oxide and 1,2-butylene oxide.

5 [0066] In the polymerization reaction, a single type of alkylene oxide may be employed, e.g. propylene oxide, in which case the product is a homopolymer, e.g. a poly(oxypropylene). However, copolymers are equally satisfactory and random copolymers are readily prepared by contacting the metal salt VI with a mixture of alkylene oxides, such as a mixture of propylene oxide and 1,2-butylene oxide, under polymerization conditions. Copolymers containing blocks of oxyalkylene units are also suitable for use in the present invention. Block copolymers may be prepared by contacting
10 the metal salt VI with first one alkylene oxide, then others in any order, or repetitively, under polymerization conditions.

[0067] The poly(oxyalkylene) alcohol V may also be prepared by living or immortal polymerization as described by S. Inoue and T. Aida in *Encyclopedia of Polymer Science and Engineering*, Second Edition, Supplemental Volume, J. Wiley and Sons, New York, pages 412-420 (1989). These procedures are especially useful for preparing poly(oxyalkylene) alcohols of formula V in which R_3 and R_4 are both alkyl groups.

15 [0068] As noted above, the alkoxide or phenoxide metal salt VI is generally derived from the corresponding hydroxy compound, $R_{12}OH$. Preferred hydroxy compounds for use in this invention include straight- or branched-chain aliphatic alcohols having 1 to about 30 carbon atoms and phenols having the formula:



25

wherein R_{13} and R_{14} are each independently hydrogen or an alkyl group having 1 to about 30 carbon atoms.

[0069] Preferably, the straight- or branched-chain aliphatic alcohols employed in this invention will contain 2 to about 22 carbon atoms, more preferably 4 to 12 carbon atoms. Representative examples of straight- or branched-chain
30 aliphatic alcohols suitable for use in this invention include, but are not limited to, n-butanol; isobutanol; sec-butanol; t-butanol; n-pentanol; n-hexanol; n-heptanol; n-octanol; isooctanol; n-nonanol; n-decanol; n-dodecanol; n-hexadecanol (cetyl alcohol); n-octadecanol (stearyl alcohol); alcohols derived from linear C_{10} to C_{30} alpha olefins and mixtures thereof; and alcohols derived from polymers of C_2 to C_6 olefins, such as alcohols derived from polypropylene and polybutene, including polypropylene alcohols having 9 to about 30 carbon atoms. Particularly preferred aliphatic alcohols
35 are butanols.

[0070] The alkylphenols of formula VIII used in this invention may be monoalkyl-substituted phenols or dialkyl-substituted phenols. Monoalkyl-substituted phenols are preferred, especially monoalkylphenols having an alkyl substituent in the *para* position.

[0071] Preferably, the alkyl group of the alkylphenols employed in this invention will contain 4 to about 24 carbon atoms, more preferably 4 to 12 carbon atoms. Representative examples of phenols suitable for use in this invention
40 include, phenol, methylphenol, dimethylphenol, ethylphenol, butylphenol, octylphenol, decylphenol, dodecylphenol, tetradecylphenol, hexadecylphenol, octadecylphenol, eicosylphenol, tetracosylphenol, hexacosylphenol, triacontylphenol and the like. Also, mixtures of alkylphenols may be employed, such as a mixture of C_{14} - C_{18} alkylphenols, a mixture of C_{18} - C_{24} alkylphenols, a mixture of C_{20} - C_{24} alkylphenols, or a mixture of C_{16} - C_{26} alkylphenols.

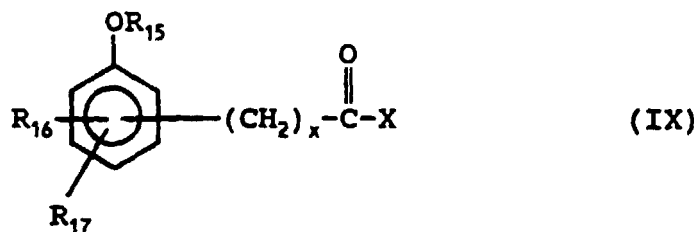
45 [0072] Particularly preferred alkylphenols are those derived from alkylation of phenol with polymers or oligomers of C_3 to C_6 olefins, such as polypropylene or polybutene. These polymers preferably contain 10 to 30 carbon atoms. An especially preferred alkylphenol is prepared by alkylating phenol with a propylene polymer having an average of 4 units. This polymer has the common name of propylene tetramer and is commercially available.

[0073] As indicated above, the poly(oxyalkylene) hydroxyaromatic esters of formula III may be prepared by esterifying a hydroxyaromatic carboxylic acid of formula IV with a poly(oxyalkylene) alcohol of formula V under conventional esterification reaction conditions.

[0074] Typically, this reaction will be conducted by contacting a poly(oxyalkylene) alcohol of formula V with about 0.25 to about 1.5 molar equivalents of a hydroxyaromatic carboxylic acid of formula IV in the presence of acidic catalyst at a temperature in the range of 70°C to about 150°C for about 0.5 to about 48 hours. Suitable acid catalysts for this
50 reaction include p-toluenesulfonic acid, methanesulfonic acid and the like. The reaction may be conducted in the presence or absence of an inert solvent, such as benzene, toluene and the like. The water generated by this reaction is preferably removed during the course of the reaction by, for example, azeotropic distillation with an inert solvent, such as toluene.

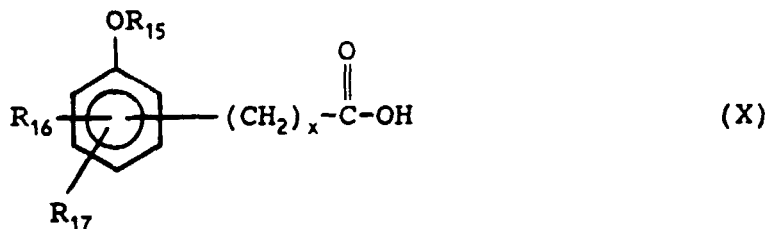
55

[0075] The poly(oxyalkylene) hydroxyaromatic esters of formula III may also be synthesized by reacting a poly(oxyalkylene) alcohol of formula V with an acyl halide having the formula:



15 wherein X is a halide, such as chloride or bromide, and R₁₅ is a suitable hydroxyl protecting group, such as benzyl, *tert*-butyldimethylsilyl, methoxymethyl, and the like; R₁₆ and R₁₇ are each independently hydrogen, lower alkyl, lower alkoxy, or the group -OR₁₈, wherein R₁₈ is a suitable hydroxyl protecting group.

[0076] Acyl halides of formula IX may be prepared from hydroxyaromatic carboxylic acids of formula IV by first protecting the aromatic hydroxyl groups of IV to form a carboxylic acid having the formula:



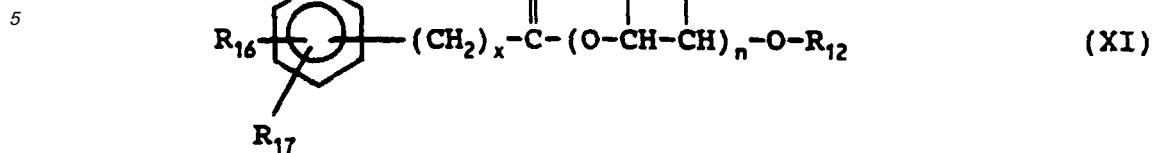
30 wherein R₁₅-R₁₇ and x are as defined above, and then converting the carboxylic acid moiety of X into an acyl halide using conventional procedures.

[0077] Protection of the aromatic hydroxyl groups of IV may be accomplished using well known procedures. The choice of a suitable protecting group for a particular hydroxyaromatic carboxylic acid will be apparent to those skilled in the art. Various protecting groups, and their introduction and removal, are described, for example, in T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Second Edition, Wiley, New York, 1991, and references cited therein. Alternatively, the protected derivatives X can be prepared from known starting materials other than the hydroxyaromatic compounds of formula IV by conventional procedures.

[0078] The carboxylic acid moiety of X may be converted into an acyl halide by contacting X with an inorganic acid halide, such as thionyl chloride, phosphorous trichloride, phosphorous tribromide, or phosphorous pentachloride; or alternatively, with oxalyl chloride. Generally, this reaction will be conducted using about 1 to 5 molar equivalents of the inorganic acid halide or oxalyl chloride, either neat or in an inert solvent, such as diethyl ether, at a temperature in the range of about 20°C to about 80°C for about 1 to about 48 hours. A catalyst, such as N,N-dimethylformamide, may also be used in this reaction.

45 **[0079]** In certain cases where the hydroxyaromatic carboxylic acids of formula IV having bulky alkyl groups adjacent to the hydroxyl group, such as 3,5-di-*t*-butyl-4-hydroxybenzoic acid, it will generally not be necessary to protect the hydroxyl group prior to formation of the acyl halide, since such hydroxyl groups are sufficiently sterically hindered so as to be substantially non-reactive with the acyl halide moiety.

[0080] Reaction of acyl halide IX with poly(oxyalkylene) alcohol V provides an intermediate poly(oxyalkylene) ester having the formula:



wherein R_3 , R_4 , R_{12} , R_{15} - R_{17} , n and x are as defined above.

[0081] Typically, this reaction is conducted by contacting V with about 0.9 to about 1.5 molar equivalents of IX in an inert solvent, such as toluene, dichloromethane, diethyl ether, and the like, at a temperature in the range of about 25°C to about 150°C. The reaction is generally complete in about 0.5 to about 48 hours. Preferably, the reaction is conducted in the presence of a sufficient amount of an amine capable of neutralizing the acid generated during the reaction, such as triethylamine, di(isopropyl)ethylamine, pyridine or 4-dimethylamino-pyridine.

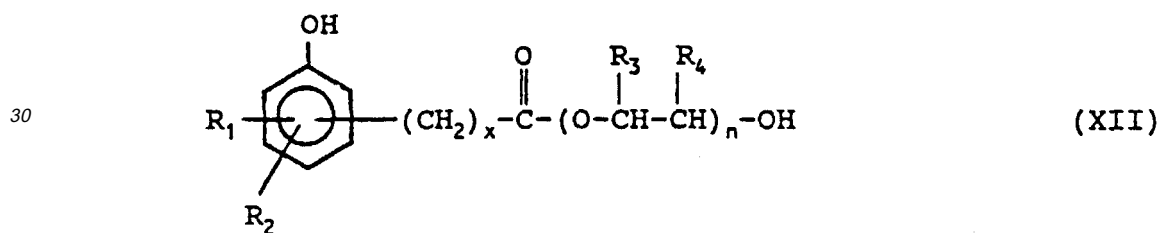
15

[0082] Deprotection of the aromatic hydroxyl group(s) of XI then provides a poly(oxyalkylene) hydroxyaromatic ester of formula III. Appropriate conditions for this deprotection step will depend upon the protecting group(s) utilized in the synthesis and will be readily apparent to those skilled in the art. For example, benzyl protecting groups may be removed by hydrogenolysis under 1 to about 4 atmospheres of hydrogen in the presence of a catalyst, such as palladium on carbon. Typically, this deprotection reaction is conducted in an inert solvent, preferably a mixture of ethyl acetate and acetic acid, at a temperature of from about 0°C to about 40°C for about 1 to about 24 hours.

20

[0083] The poly(oxyalkylene) hydroxyaromatic esters of the present invention or for use in the present invention having the formula:

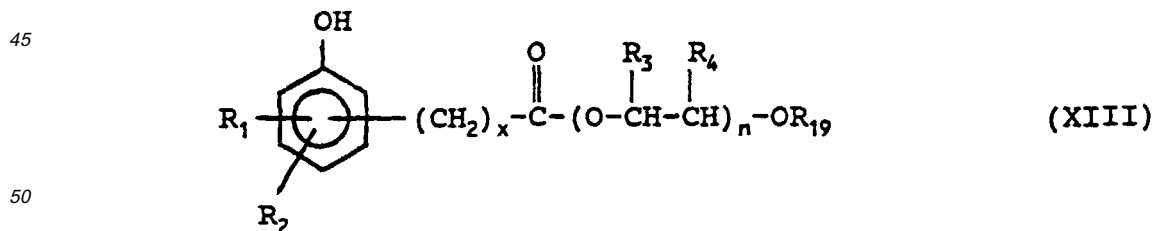
25



wherein R_1 - R_4 , n and x are as defined above, can be prepared from compounds of formula III or XI, wherein R_{12} is a benzyl group, by removing the benzyl group using conventional hydrogenolysis procedures. Compounds of formula III or XI where R_{12} represents a benzyl group may be prepared by employing a metal salt VI derived from benzyl alcohol in the above described synthetic procedures.

40

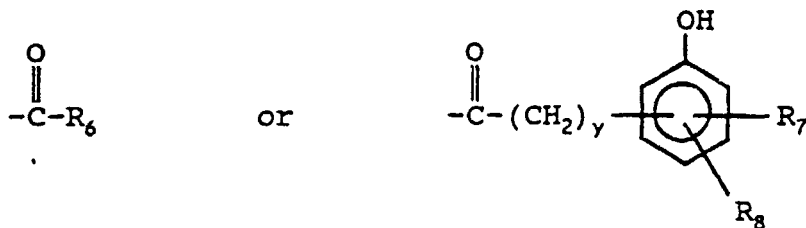
[0084] Similarly, the poly(oxyalkylene) hydroxyaromatic esters of the present invention or for use in the present invention having the formula:



wherein R_1 - R_4 , n and x are as defined above and R_{19} is an acyl group having the formula:

55

5



10

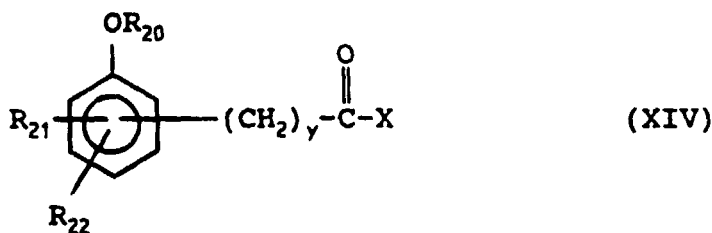
wherein R_6 - R_8 and y are as defined above, can be synthesized in several steps from a compound of formula XI, wherein R_{12} represents a benzyl group and R_{15} (and optionally R_{18}) represents a hydroxyl protecting group that is stable to hydrogenolysis conditions, such as a *tert*-butyldimethylsilyl group. The synthesis of XIII from such compounds may be effected by first removing the benzyl group using conventional hydrogenolysis conditions and then acylating the resulting hydroxyl group with a suitable acylating agent. Removal of the protecting group(s) from the aromatic hydroxyl group(s) using conventional procedures then provides a poly(oxyalkylene) hydroxyaromatic ester of formula XIII.

15

20

[0085] Suitable acylating agents for use in this reaction include acyl halides, such as acyl chlorides and bromides; and carboxylic acid anhydrides. Preferred acylating agents are those having the formula: $\text{R}_6\text{C}(\text{O})-\text{X}$, wherein R_6 is alkyl having 1 to 30 carbon atom, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms, and X is chloro or bromo; and those having the formula:

25



30

wherein X is a halide, such as chloride or bromide, R_{20} is a suitable hydroxyl protecting group, R_{21} and R_{22} are each independently hydrogen, lower alkyl, lower alkoxy, or the group $-\text{OR}_{23}$, wherein R_{23} is a suitable hydroxyl protecting group, and y is an integer from 0 to 10.

35

[0086] A particularly preferred group of acylating agents are those having the formula: $\text{R}_{24}\text{C}(\text{O})-\text{X}$, wherein R_{24} is alkyl having 4 to 12 carbon atoms. Representative examples of such acylating agents include acetyl chloride, propionyl chloride, butanoyl chloride, pivaloyl chloride, octanoyl chloride, decanoyl chloride and the like.

40

[0087] Another particularly preferred group of acylating agents are those of formula XIV, wherein R_{20} is benzyl; R_{21} is hydrogen, alkyl having 1 to 4 carbon atoms, or $-\text{OR}_{25}$, wherein R_{25} is a suitable hydroxyl protecting group, preferably benzyl; R_{22} is hydrogen; and y is 0, 1 or 2. Representative examples of such acylating agents include 4-benzyloxybenzoyl chloride, 3-benzyloxybenzoyl chloride, 4-benzyloxy-3-methylbenzoyl chloride, 4-benzyloxyphenylacetyl chloride, 3-(4-benzyloxyphenyl)propionyl chloride and the like.

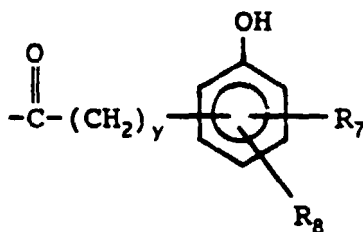
45

[0088] Generally, this acylation reaction will be conducted using about 0.95 to about 1.2 molar equivalents of the acylating agent. The reaction is typically conducted in an inert solvent, such as toluene, dichloromethane, diethyl ether and the like, at a temperature in the range of about 25°C to about 150°C for about 0.5 to about 48 hours. When an acyl halide is employed as the acylating agent, the reaction is preferably conducted in the presence of a sufficient amount of an amine capable of neutralizing the acid generated during the reaction, such as triethylamine, di(isopropyl)ethylamine, pyridine or 4-dimethylaminopyridine.

50

[0089] A particularly preferred group of poly(oxyalkylene) hydroxyaromatic esters of formula XIII are those having the same hydroxyaromatic ester group at each end the poly(oxyalkylene) moiety, i.e. compounds of formula XIII wherein R_{19} is an acyl group having the formula:

55



wherein R_7 is the same group as R_1 , R_8 is the same group as R_2 , and x and y are the same integer.

[0090] These compounds may be prepared from a poly(oxyalkylene) diol having the formula:



wherein R_3 , R_4 , and n are as defined above, by esterifying each of the hydroxyl groups present in XV with a hydroxyaromatic carboxylic acid of formula IV or an acyl halide of formula IX using the above described synthetic procedures. The poly(oxyalkylene) diols of formula XV are commercially available or may be prepared by conventional procedures, for example, by using sodium or potassium hydroxide in place of the alkoxide or phenoxide metal salt VI in the above described alkylene oxide polymerization reaction.

25

Fuel Compositions

[0091] The poly(oxyalkylene) hydroxyaromatic esters of the present invention are useful as additives in hydrocarbon fuels to prevent and control engine deposits, particularly intake valve deposits. The proper concentration of additive necessary to achieve the desired deposit control varies depending upon the type of fuel employed, the type of engine, and the presence of other fuel additives.

30

[0092] In general, the concentration of the poly(oxyalkylene) hydroxyaromatic esters of this invention in hydrocarbon fuel will range from about 50 to about 2500 parts per million (ppm) by weight, preferably from 75 to 1,000 ppm.

When other deposit control additives are present, a lesser amount of the present additive may be used.

35

[0093] The poly(oxyalkylene) hydroxyaromatic esters of the present invention may be formulated as a concentrate using an inert stable oleophilic (i.e., dissolves in gasoline) organic solvent boiling in the range of about 65°C to 250°C (150°F to 400°F). Preferably, an aliphatic or an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols containing about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol and the like, in combination with hydrocarbon solvents are also suitable for use with the present additives. In the concentrate, the amount of the additive will generally range from about 10 to about 70 weight percent, preferably 10 to 50 weight percent, more preferably from 20 to 40 weight percent.

40

[0094] In gasoline fuels, other fuel additives may be employed with the additives of the present invention, including, for example, oxygenates, such as t-butyl methyl ether, antiknock agents, such as methylcyclopentadienyl manganese tricarbonyl, and other dispersants/detergents, such as hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or succinimides. Additionally, antioxidants, metal deactivators and demulsifiers may be present.

45

[0095] In diesel fuels, other well-known additives can be employed, such as pour point depressants, flow improvers, cetane improvers, and the like.

[0096] A fuel-soluble, nonvolatile carrier fluid or oil may also be used with the poly(oxyalkylene) hydroxyaromatic esters of this invention. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the nonvolatile residue (NVR), or solvent-free liquid fraction of the fuel additive composition while not overwhelmingly contributing to octane requirement increase.

50

[0097] The carrier fluid may be a natural or synthetic oil, such as mineral oil, refined petroleum oils, synthetic polyalkanes and alkenes, including hydrogenated and unhydrogenated polyalphaolefins, and synthetic polyoxyalkylene-derived oils, such as those described, for example, in U.S. Patent No. 4,191,537 to Lewis.

55

[0098] These carrier fluids are believed to act as a carrier for the fuel additives of the present invention and to assist in removing and retarding deposits. The carrier fluid may also exhibit synergistic deposit control properties when used in combination with a hydroxyaromatic poly(oxyalkylene) compound of this invention.

[0099] The carrier fluids are typically employed in amounts ranging from about 100 to about 5000 ppm by weight of the hydrocarbon fuel, preferably from 400 to 3000 ppm of the fuel. Preferably, the ratio of carrier fluid to deposit control additive will range from about 0.5:1 to about 10:1, more preferably from 1:1 to 4:1, most preferably about 2:1.

[0100] When employed in a fuel concentrate, carrier fluids will generally be present in amounts ranging from about 20 to about 60 weight percent, preferably from 30 to 50 weight percent.

EXAMPLES

[0101] The following examples are presented to illustrate specific embodiments of the present invention and synthetic preparations thereof; and should not be interpreted as limitations upon the scope of the invention.

Example 1

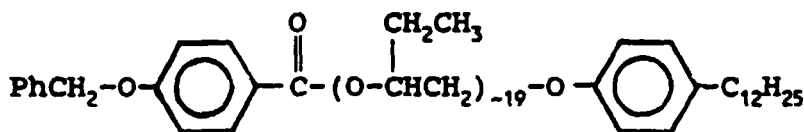
Preparation of 4-Benzyloxybenzoyl Chloride

[0102] To a flask equipped with a magnetic stirrer and drying tube was added 10.0 grams of 4-benzyloxybenzoic acid and 100 mL of anhydrous diethyl ether and then 19.1 mL of oxalyl chloride. The resulting mixture was stirred at room temperature for 16 hours and then the solvent was removed *in vacuo* to yield 10.8 grams of the desired acid chloride.

Example 2

Preparation of α -(4-Benzyloxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

[0103]

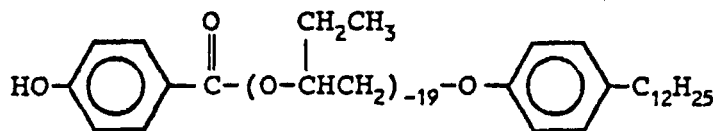


[0104] 4-Benzyloxybenzoyl chloride (10.8 grams) from Example 1 was combined with 72.2 grams of α -hydroxy- ω -4-dodecylphenoxy poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 150 mL of anhydrous toluene. Triethylamine (6.41 mL) and 4-dimethylaminopyridine (0.54 grams) were then added and the resulting mixture was heated to reflux under nitrogen for 16 hours. The reaction was then cooled to room temperature and diluted with 300 mL of diethyl ether. The organic layer was washed twice with 1% aqueous hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 76.5 grams of a light brown oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether/ethanol (8:1.5:0.5), to yield 43.2 grams of the desired product as a colorless oil.

Example 3

Preparation of α -(4-Hydroxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

5 [0105]



10

15

[0106] A solution of 15.9 grams of the product from Example 2 in 50 mL of ethyl acetate and 50 mL of acetic acid containing 3.48 grams of 5% palladium on charcoal was hydrogenolyzed at 241-276 kPa (35-40 psi) for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of residual acetic acid with toluene *in vacuo* yielded 14.6 grams of the desired product as a colorless oil. The product had an average of 19 oxybutylene units. IR (neat) 1715 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.9, 7.3 (AB quartet, 4H), 7.1-7.25 (m, 2H), 6.7-6.9 (m, 2H), 5.05-5.15 (m, 1H), 3.1-4.0 (m, 56H), 0.5-1.9 (m, 120H).

20

[0107] Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

25

- α -(4-hydroxybenzoyl)- ω -n-butyloxy poly(oxybutylene);
- α -(4-hydroxybenzoyl)- ω -4-t-butylphenoxy poly(oxybutylene);
- α -(4-hydroxybenzoyl)- ω -4-octacosylphenoxy poly(oxybutylene);
- α -(4-hydroxy-3-methoxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene);
- α -(4-hydroxy-3-methylbenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene); and
- α -(3,4-dihydroxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene).

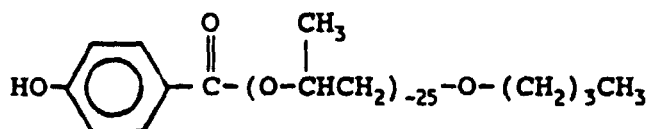
30

Example 4

Preparation of α -(4-Hydroxybenzoyl)- ω -n-butoxy poly(oxypropylene)

35

[0108]



40

45

[0109] To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, nitrogen inlet and reflux condenser was added 4.52 grams of 4-hydroxybenzoic acid, 50.0 grams of α -hydroxy- ω -n-butoxy poly(oxypropylene) having an average of 25 oxypropylene units (commercially available from Union Carbide as LB385) and 0.56 grams of p-toluenesulfonic acid. The reaction was heated to 120°C for 16 hours and then cooled to room temperature. Diethyl ether (750 mL) was added and the organic phase was washed twice with saturated aqueous sodium bicarbonate, and once with saturated aqueous sodium chloride solution. The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford 51.7 grams of a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (49:49:2) to yield 25.2 grams of the desired product as a yellow oil. The product had an average of 25 oxypropylene units IR (neat) 1715 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.9, 6.85 (AB quartet, 4H), 5.05-5.15 (m, 1H), 3.1-4.0 (m, 76H), 1.4-1.6 (m, 2H), 1.25-1.4 (m, 2H), 0.9-1.4 (m, 75H), 0.75-0.9 (t, 3H).

55

[0110] Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

α -(4-hydroxybenzoyl)- ω -4-t-butylphenoxypropyl(oxypropylene);
 α -(4-hydroxybenzoyl)- ω -4-dodecylphenoxypropyl(oxypropylene);
 α -(4-hydroxy-3-methoxybenzoyl)- ω -n-butoxypropyl(oxypropylene);
 α -(4-hydroxy-3-methylbenzoyl)- ω -n-butoxypropyl(oxypropylene);
 and
 α -(3,4-dihydroxybenzoyl)- ω -n-butoxypropyl(oxybutylene).

Example 5

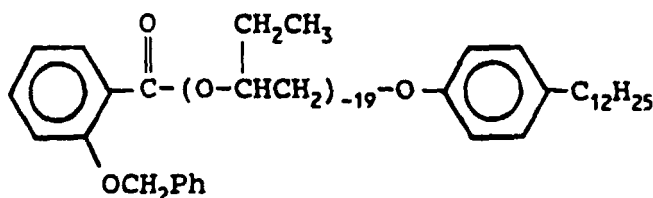
10 Preparation of 2-Benzyloxybenzoyl Chloride

[0111] To a flask equipped with a magnetic stirrer and drying tube was added 15.0 grams of 2-benzyloxybenzoic acid and 150 mL of anhydrous dichloromethane followed by 28.7 mL of oxalyl chloride. The reaction was stirred at room temperature for 16 hours, and then the solvent was removed *in vacuo* to yield 16.2 grams of the desired acid chloride.

Example 6

Preparation of α -(2-Benzyloxybenzoyl)- ω -4-dodecylphenoxypropyl(oxybutylene)

20 [0112]

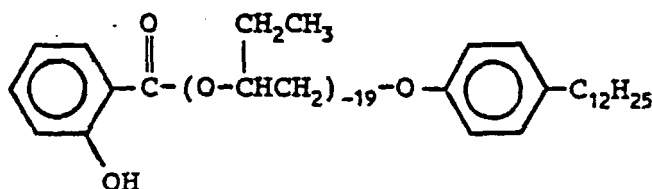


[0113] 2-Benzyloxybenzoyl chloride (16.2 grams) from Example 5 was combined with 108.3 grams of α -hydroxy- ω -4-dodecylphenoxypropyl(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 225 mL of anhydrous toluene. Triethylamine (9.6 mL) and 4-dimethylaminopyridine (0.8 grams) were added and the reaction was heated to reflux under nitrogen for 16 hours, then cooled to room temperature and diluted with 500 mL of diethyl ether. The organic layer was washed twice with 1% aqueous hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to yield 119.2 grams of a light brown oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether/ethanol (8:1.5:0.5) to yield 73.0 grams of the desired product as a light brown oil.

Example 7

Preparation of α -(2-Hydroxybenzoyl)- ω -4-dodecylphenoxypropyl(oxybutylene)

45 [0114]



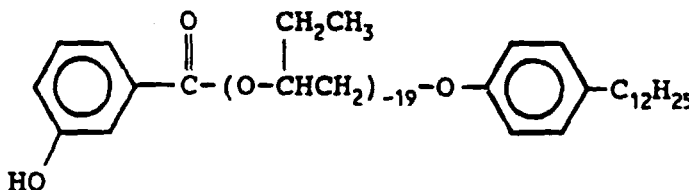
[0115] A solution of 30.8 grams of the product from Example 6 in 95 mL of ethyl acetate and 95 mL of acetic acid

containing 3.39 grams of 10% palladium on charcoal was hydrogenolyzed at 241-276 kPa (35-40 psi) for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of solvent *in vacuo* followed by azeotropic removal of residual acetic acid with toluene under vacuum yielded 28.9 grams of the desired product as a light brown oil. The product had an average of 19 oxybutylene units. IR (neat) 1673 cm^{-1} , ^1H NMR (CDCl_3) δ 10.85 (s, 1H), 7.8-8.2 (m, 8H), 5.1-5.3 (m, 1H), 3.2-4.1 (m, 56H), 0.5-1.9 (m, 21H).

Example 8

Preparation of α -(3-Hydroxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

[0116]



[0117] To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, nitrogen inlet and reflux condenser was added 5.08 grams of 3-hydroxybenzoic acid, 50.0 grams of α -hydroxy- ω -4-dodecylphenoxy-poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 0.53 grams of p-toluenesulfonic acid. The reaction was heated to 130°C for 48 hours and then cooled to room temperature. Diethyl ether (750 mL) was added and the organic phase was washed twice with saturated aqueous sodium bicarbonate and once with saturated aqueous sodium chloride solution. The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford 47.8 grams of a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (78:20:2) to yield 16.5 grams of the desired product as a yellow oil. The product had an average of 19 oxybutylene groups. IR (neat) 1716 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.6-7.6 (m, 8H), 4.9-5.2 (m, 1H), 3.1-4.0 (m, 56H), 0.5-1.9 (m, 21H).

Example 9

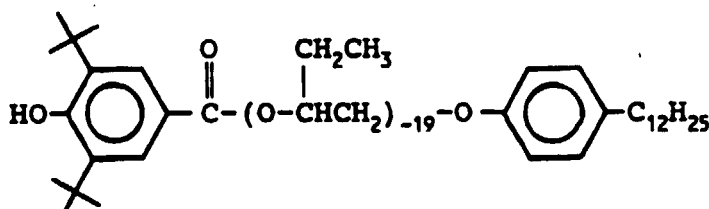
Preparation of 3,5-Di-t-butyl-4-hydroxybenzoyl Chloride

[0118] To a flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet was added 1.88 grams of 3,5-di-t-butyl-4-hydroxybenzoic acid and 15 mL of thionyl chloride. The reaction was refluxed for 2 hours and stirred at room temperature for 16 hours. The excess thionyl chloride was removed *in vacuo* to yield 2.2 grams of the desired acid chloride as a white solid.

Example 10

Preparation of α -(3,5-Di-t-butyl-4-hydroxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

[0119]



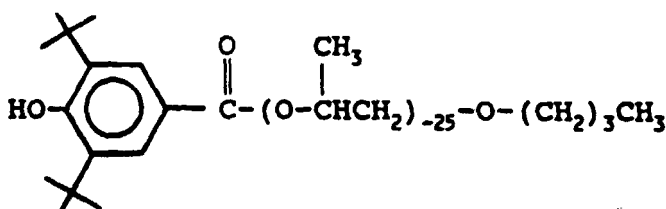
[0120] 3,5-Di-t-butyl-4-hydroxybenzoyl chloride (2.2 grams) from Example 9 was combined with 13.6 grams of α -

hydroxy- ω -4-dodecylphenoxy-poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 50 mL of anhydrous toluene. Triethylamine (1.17 mL) and 4-dimethylaminopyridine (0.1 grams) were added and the reaction was heated to reflux under nitrogen for 16 hours, and then cooled to room temperature and diluted with 100 mL of hexane. The organic layer was washed twice with water, once with saturated aqueous sodium bicarbonate solution and once with saturated aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to give an oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether/ethanol (6:3.5:0.5) to yield 3.0 grams of the desired product as a yellow oil. IR (neat) 1715 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.8 (s, 2H), 7.1-7.25 (m, 2H), 6.7-6.9 (m, 2H), 5.7 (s, 1H), 7.1-7.25 (m, 2H), 6.7-6.9 (m, 2H), 5.7 (s, 1H), 5.05-5.15 (m, 1H), 3.1-4.0 (m, 56H), 0.5-1.9 (m, 138H).

Example 11

Preparation of α -(3,5-Di-*t*-butyl-4-hydroxybenzoyl)- ω -*n*-butoxypoly(oxypropylene)

[0121]

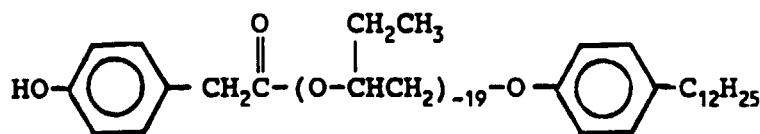


[0122] 3,5-Di-*t*-butyl-4-hydroxybenzoyl chloride (8.0 grams) prepared as described in Example 9 was combined with 46.2 grams of α -hydroxy- ω -*n*-butoxypoly(oxypropylene) having an average of 25 oxypropylene units (commercially available from Union Carbide as LB385) and 200 mL of anhydrous toluene. Triethylamine (4.4 mL) and 4-dimethylaminopyridine (0.37 grams) were added and the reaction was heated to reflux under nitrogen for 16 hours, and then cooled to room temperature and diluted with 500 mL of hexane. The organic layer was washed twice with water, once with saturated aqueous sodium bicarbonate solution and once with saturated aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to give an oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether/ethanol (6:3.5:0.5) to yield 42.0 grams of the desired product as a yellow oil. The product had an average of 25 oxypropylene units. IR (neat) 1715 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.8 (s, 2H), 5.7 (s, 1H), 5.05-5.15 (m, 1H), 3.2-3.9 (m, 75H), 0.9-1.6 (m, 97H), 0.75-0.9 (t, 3H).

Example 12

Preparation of α -[(4-Hydroxyphenyl)acetyl]- ω -4-dodecylphenoxy-poly(oxybutylene)

[0123]



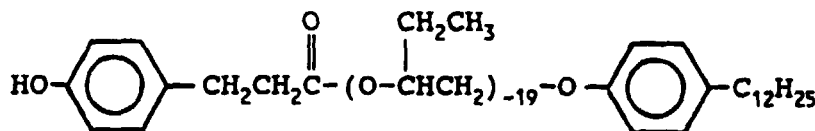
[0124] To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, nitrogen inlet and reflux condenser was added 4.66 grams of 4-hydroxyphenylacetic acid, 50.0 grams of α -hydroxy- ω -4-dodecylphenoxy-poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 0.63 grams of *p*-toluenesulfonic acid. The reaction was heated to 120°C for 16 hours and then cooled to room temperature. Diethyl ether (750 mL) was added and the organic phase was washed twice with saturated aqueous

ous sodium bicarbonate, and then once with saturated aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford 51.6 grams of a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (93:5:2) to yield 26.2 grams of the desired product as a yellow oil. The product had an average of 19 oxybutylene units. IR (neat) 1742 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.7-7.25 (m, 8H), 4.8-5.0 (m, 1H), 3.1-4.05 (m, 58H), 0.5-1.9 (m, 120H).

Example 13

Preparation of α -[3-(4-Hydroxyphenyl)propionyl]- ω -4-dodecylphenoxy poly(oxybutylene)

[0125]

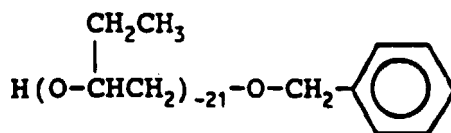


[0126] To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, nitrogen inlet and reflux condenser was added 5.09 grams of 3-(4-hydroxyphenyl)propionic acid, 50.0 grams of α -hydroxy- ω -4-dodecylphenoxy poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 0.63 grams of p-toluenesulfonic acid. The reaction was heated to 120°C for 16 hours and then cooled to room temperature. Diethyl ether (750 mL) was added and the organic phase was washed twice with saturated aqueous sodium bicarbonate, and once with saturated aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford 52.7 grams of a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (93:5:2) to yield 37.5 grams of the desired product as a yellow oil. IR (neat) 1735 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.7-7.25 (m, 8H), 4.8-5.0 (m, 1H), 3.1-4.05 (m, 56H), 2.9 (t, 2H), 2.55 (t, 2H), 0.5-0.9 (m, 120H).

Example 14

Preparation of α -Benzyloxy- ω -4-hydroxypoly(oxybutylene)

[0127]



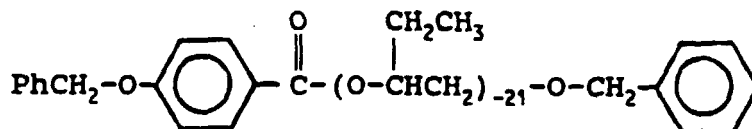
[0128] To a flask equipped with a mechanical stirrer, thermometer, addition funnel, reflux condenser and nitrogen inlet was added 1.59 grams of a 35 wt. % dispersion of potassium hydride in mineral oil. Benzyl alcohol (5.0 grams) dissolved in 250 mL of anhydrous toluene was added dropwise. After hydrogen evolution had subsided, the reaction was heated to reflux for 3 hours and then cooled to room temperature. 1,2-Epoxybutane (99.6 mL) were then added dropwise and the reaction was refluxed for 16 hours. The reaction was cooled to room temperature, quenched with 5 mL of methanol and diluted with 500 mL of diethyl ether. The resulting mixture was washed with saturated aqueous ammonium chloride, followed by water and saturated aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 64.1 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (90:8:2) to afford 40 grams of the desired product as a light yellow oil.

Example 15

Preparation of α -(4-Benzyloxybenzoyl)- ω -benzyloxypoly(oxybutylene)

5 [0129]

10



15

20

[0130] 4-Benzyloxybenzoyl chloride (10.8 grams) from Example 1 was combined with α -benzyloxy- ω -hydroxypoly(oxybutylene) (15.0 grams) from Example 14 and 50 mL of anhydrous toluene. Triethylamine (1.3 mL) and 4-dimethylaminopyridine (0.55 grams) were then added and the resulting mixture was heated to reflux under nitrogen for 16 hours. The reaction was then cooled to room temperature and diluted with 100 mL of diethyl ether. The organic layer was washed twice with 1% aqueous hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 16.8 grams of the desired product as a yellow oil.

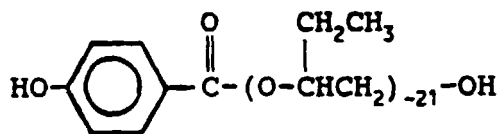
Example 16

25

Preparation of α -(4-Hydroxybenzoyl)- ω -hydroxypoly(oxybutylene)

[0131]

30



35

40

[0132] A solution of 16.8 grams of the product from Example 15 in 100 mL of ethyl acetate and 100 mL of acetic acid containing 3.0 grams of 5% palladium on charcoal was hydrogenolyzed at 241-276 kPa (35-40 psi) for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of residual acetic acid with toluene *in vacuo* yielded 14.8 grams of the desired product as a yellow oil. The product had an average of 21 oxybutylene units. IR (neat) 1715 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.9, 6.8 (AB quartet, 4H), 5.05-5.15 (m, 1H), 3.1-3.9 (m, 62H), 0.6-1.9 (m, 105H).

45 Comparative Example A

Preparation of Polyisobutylphenol

50

55

[0133] To a flask equipped with a magnetic stirrer, reflux condenser, thermometer, addition funnel and nitrogen inlet was added 203.2 grams of phenol. The phenol was warmed to 40°C and boron trifluoride etherate (73.5 mL) was added dropwise. Ultravis 10 polyisobutene (1040 grams, molecular weight 950, 76% methylvinylidene isomer, available from British Petroleum), dissolved in 1,863 mL of hexane, was then added to the reaction mixture at a rate sufficient to maintain the temperature between 22-27°C. The reaction mixture was then stirred for 16 hours at room temperature. Concentrated ammonium hydroxide (400 mL) was then added and the mixture was diluted with 2 L of hexane. The resulting mixture was washed with water (3 x 2 L), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo* to yield 1,056.5 grams of an oil. This oil was determined to contain 80% of the desired polyisobutenylphenol and 20% polyisobutene by ^1H NMR and also by chromatography on silica gel, eluting first with hexane and then with hexane/ethyl acetate/ethanol (93:5:2).

Example 17

Single-Cylinder Engine Test

5 [0134] The test compounds were blended in gasoline and their deposit reducing capacity determined in an ASTM/CFR single-cylinder engine test.

[0135] A Waukesha CFR single-cylinder engine was used. Each run was carried out for 15 hours, at the end of which time the intake valve was removed, washed with hexane and weighed. The previously determined weight of the clean valve was subtracted from the weight of the valve at the end of the run. The differences between the two weights is the weight of the deposit. A lesser amount of deposit indicates a superior additive. The operating conditions of the test were as follows: water jacket temperature 93°C (200°F); vacuum of 305 mmHg (12 in Hg), air-fuel ratio of 12, ignition spark, timing of 40° BTC; engine speed is 1800 rpm; the crankcase oil is a commercial 30W oil.

10 [0136] The amount of carbonaceous deposit in milligrams on the intake valves is reported for each of the test compounds in Table I.

TABLE I

Sample ¹	Intake Valve Deposit Weight (in milligrams)		
	Run 1	Run 2	Average
Base Fuel	214.7	193.7	204.2
Example 3	7.1	9.1	8.1
Example 4	127.7	128.4	128.1
Example 7	150.0	215.4	182.7
Example 8	62.3	57.5	59.9
Example 10	108.0	95.1	101.6
Example 11	117.1	124.6	120.9
Example 12	84.6	98.4	91.5
Example 13	90.5	90.7	90.6
Example 16	41.1	43.0	42.1

¹ At 200 parts per million actives (ppma).

[0137] The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

[0138] The data in Table I illustrates the significant reduction in intake valve deposits provided by the poly(oxyalkylene) hydroxyaromatic esters of the present invention (Examples 3, 7, 8, 10, 12, 16) or used in the present invention (Examples 4 and 11) compared to the base fuel.

45 Example 18

Multicylinder Engine Test

[0139] The poly(oxyalkylene) hydroxyaromatic esters of the present invention were tested in a laboratory multicylinder engine to evaluate their intake valve and combustion chamber deposit control performance. The test engine was a 4.3 liter, TBI (throttle body injected), V6 engine manufactured by General Motors Corporation.

[0140] The major engine dimensions are set forth in Table II:

Table II

Engine Dimensions	
Bore	10.16 cm

EP 0 636 164 B1

Table II (continued)

Engine Dimensions	
Stroke	8.84 cm
Displacement Volume	4.3 liter
Compression Ratio	9.3:1

5

[0141] The test engine was operated for 40 hours (24 hours a day) on a prescribed load and speed schedule representative of typical driving conditions. The cycle for engine operation during the test is set forth in Table III.

10

Table III

Engine Driving Cycle				
Step	Mode	Time in Mode [Sec] ¹	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

15

20

25

¹ All steps, except step number 3, include a 15 second transition ramp. Step 3 includes a 20 second transition ramp.

30

[0142] All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table IV.

35

Table IV

Multicylinder Engine Test Results			
Sample ¹		Intake Valve Deposits ²	Combustion Chamber Deposits ²
Base Fuel	Run 1	951	1887
	Run 2	993	1916
	Average	972	1902
Example 3	Run 1	48	2173
	Run 2	48	2205
	Average	48	2189
Comparative Example A	Run 1	229	2699
	Run 2	218	2738
	Average	224	2719

40

45

50

¹ At 400 parts per million actives (ppma).

² In milligrams (mg).

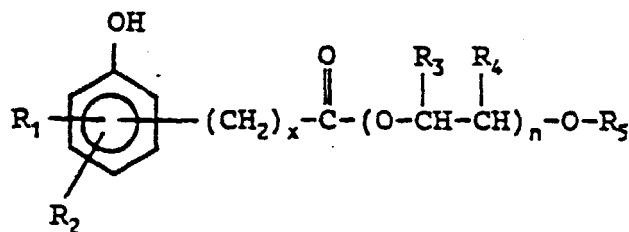
55

[0143] The base fuel employed in the above multicylinder engine tests contained no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 400 ppma (parts per million actives).

[0144] The data in Table IV illustrates the significant reduction in intake valve deposits provided by the poly(oxy-alkylene) hydroxyaromatic esters of the present invention (Example 3) compared to the base fuel. Moreover, the data in Table IV further demonstrates the significant reduction in combustion chamber deposits produced by the poly(oxy-alkylene) hydroxyaromatic ethers of the present invention (Example 3) compared to a known polyisobutylphenol fuel additive (Comparative Example A).

Claims

1. The use of compound of the formula:

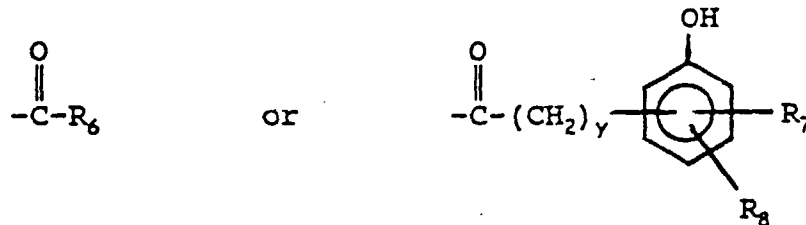


or a fuel-soluble salt thereof; wherein

R_1 and R_2 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R_3 and R_4 are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_5 is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group having the formula:



wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; R_7 and R_8 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

n is an integer from 5 to 100; and x and y are each independently an integer from 0 to 10;

as an additive in a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range, for the control of engine deposits.

2. The use according to Claim 1, wherein n is an integer ranging from 10 to 50.

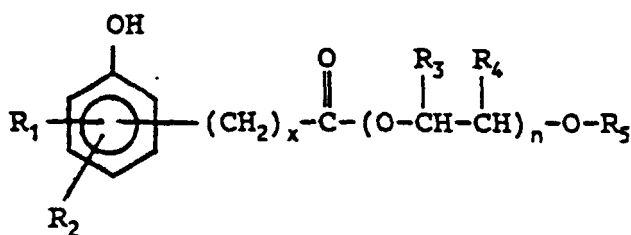
3. The use according to Claim 2, wherein n is an integer ranging from 15 to 30.

4. The use according to Claim 2, wherein R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; and R_2 is hydrogen.

5. The use according to Claim 4, wherein R_5 is hydrogen, alkyl having 2 to 22 carbon atoms, or alkylphenyl having an alkyl group containing 4 to 24 carbon atoms.

6. The use according to Claim 5, wherein R_1 is hydrogen or hydroxy.

7. The use according to Claim 6, wherein R₅ is hydrogen, alkyl having 4 to 12 carbon atoms, or alkylphenyl having an alkyl group containing 4 to 12 carbon atoms.
8. The use according to Claim 7, wherein one of R₃ and R₄ is lower alkyl having 1 to 3 carbon atoms and the other is hydrogen.
9. The use according to Claim 8, wherein one of R₃ and R₄ is methyl or ethyl and the other is hydrogen.
10. The use according to Claim 9, wherein x is 0, 1 or 2.
11. The use according to Claim 10, wherein R₁ is hydrogen, R₅ is alkylphenyl having an alkyl group containing 4 to 12 carbon atoms, and x is 0.
12. A compound of the formula:

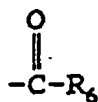


or a fuel-soluble salt thereof; wherein

R₁ and R₂ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R₃ and R₄ are each hydrogen or ethyl, wherein one of R₃ and R₄ is ethyl and the other is hydrogen;

R₅ is hydrogen, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group having the formula:

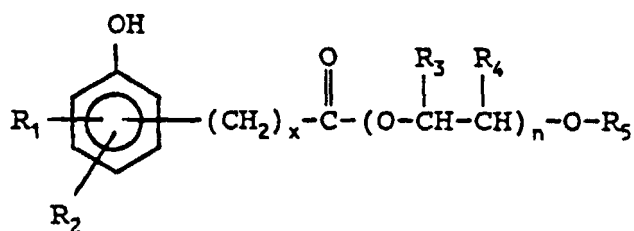


wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; n is an integer from 10 to 50; and x is an integer from 0 to 10.

13. The compound according to claim 12, wherein n is an integer ranging from 15 to 30.
14. The compound according to Claim 12, wherein R₁ is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; and R₂ is hydrogen.
15. The compound according to Claim 14, wherein R₅ is hydrogen or alkylphenyl having an alkyl group containing 4 to 24 carbon atoms.
16. The compound according to Claim 15, wherein R₁ is hydrogen or hydroxy.
17. The compound according to Claim 16, wherein R₅ is hydrogen or alkylphenyl having an alkyl group containing 4 to 12 carbon atoms.
18. The compound according to Claim 17, wherein x is 0, 1 or 2.
19. The compound according to Claim 18, wherein R₁ is hydrogen, R₅ is alkylphenyl having an alkyl group containing

4 to 12 carbon atoms, and x is 0.

20. A fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an effective detergent amount of a compound of the formula:

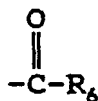


or a fuel-soluble salt thereof; wherein

R₁ and R₂ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R₃ and R₄ are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

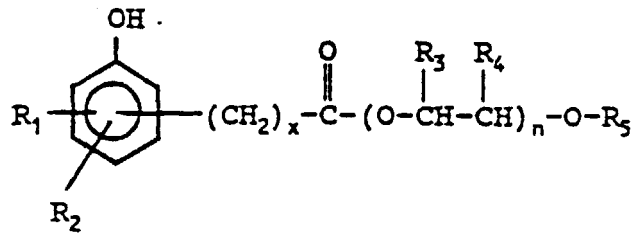
R₅ is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:



wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms;

n is an integer from 10 to 50; and x is an integer from 0 to 10.

21. The fuel composition according to Claim 20, wherein R₁ is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; R₂ is hydrogen; one of R₃ and R₄ is hydrogen and the other is methyl or ethyl; R₅ is hydrogen, alkyl having 2 to 22 carbon atoms, or alkylphenyl having an alkyl group containing 4 to 24 carbon atoms; n is 15 to 30 and x is 0, 1 or 2.
22. The fuel composition according to Claim 21, wherein R₁ is hydrogen or hydroxy; R₅ is hydrogen, alkyl having 4 to 12 carbon atoms, or alkylphenyl having an alkyl group containing 4 to 12 carbon atoms; and x is 0.
23. The fuel composition according to Claim 22, wherein R₁ is hydrogen, and R₅ is alkylphenyl having an alkyl group containing 4 to 12 carbon atoms.
24. The fuel composition according to Claim 20, wherein said composition contains about 50 to about 2500 parts per million by weight of said compound.
25. A fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 66°C to 200°C (150°F to 400°F) and from about 10 to about 70 weight percent of a compound of the formula:

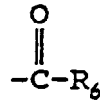


or a fuel-soluble salt thereof; wherein

15 R₁ and R₂ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R₃ and R₄ are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

20 R₅ is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:



30 wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms;

n is an integer from 10 to 50; and x is an integer from 0 to 10.

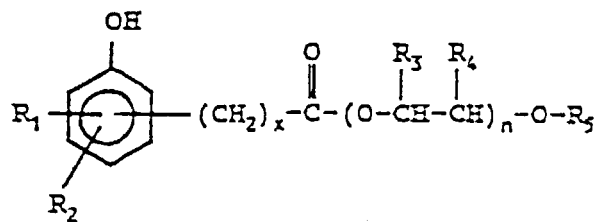
35 **26.** The fuel concentrate according to Claim 25, wherein R₁ is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; R₂ is hydrogen; one of R₃ and R₄ is hydrogen and the other is methyl or ethyl; R₅ is hydrogen, alkyl having 2 to 22 carbon atoms, or alkylphenyl having an alkyl group containing 4 to 24 carbon atoms; n is 15 to 30 and x is 0, 1 or 2.

40 **27.** The fuel concentrate according to Claim 26, wherein R₁ is hydrogen or hydroxy; R₅ is hydrogen, alkyl having 4 to 12 carbon atoms, or alkylphenyl having an alkyl group containing 4 to 12 carbon atoms; and x is 0.

45 **28.** The fuel concentrate according to Claim 27, wherein R₁ is hydrogen, and R₅ is alkylphenyl having an alkyl group containing 4 to 12 carbon atoms.

Patentansprüche

50 **1.** Verwendung der Verbindung der Formel:

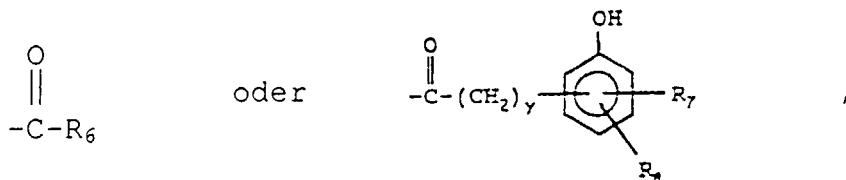


oder eines kraftstofflöslichen Salzes davon; wobei

R₁ und R₂ jeweils unabhängig voneinander Wasserstoff, Hydroxy, Niederalkyl mit 1 bis 6 Kohlenstoffatomen oder Niederalkoxy mit 1 bis 6 Kohlenstoffatomen sind;

R₃ und R₄ jeweils unabhängig voneinander Wasserstoff oder Niederalkyl mit 1 bis 6 Kohlenstoffatomen sind;

R₅ Wasserstoff, Alkyl mit 1 bis 30 Kohlenstoffatomen, Phenyl, Aralkyl oder Alkaryl mit 7 bis 36 Kohlenstoffatomen oder ein Acylrest ist der Formel:



wobei R₆ Alkyl mit 1 bis 30 Kohlenstoffatomen, Phenyl oder Aralkyl oder Alkaryl mit 7 bis 36 Kohlenstoffatomen ist;

R₇ und R₈ jeweils unabhängig voneinander Wasserstoff, Hydroxy, Niederalkyl mit 1 bis 6 Kohlenstoffatomen oder Niederalkoxy mit 1 bis 6 Kohlenstoffatomen sind;

n eine ganze Zahl von 5 bis 100 ist; und x und y jeweils unabhängig voneinander eine ganze Zahl von 0 bis 10 sind;

als Additiv in einer Kraftstoffzusammensetzung, umfassend eine größere Menge an Kohlenwasserstoffen des Benzin- oder Dieselsiedebereichs, zur Bekämpfung von Motorablagerungen.

2. Verwendung nach Anspruch 1, wobei n eine ganze Zahl von 10 bis 50 ist.

3. Verwendung nach Anspruch 2, wobei n eine ganze Zahl von 15 bis 30 ist.

4. Verwendung nach Anspruch 2, wobei R₁ Wasserstoff, Hydroxy oder Niederalkyl mit 1 bis 4 Kohlenstoffatomen ist; und R₂ Wasserstoff ist.

5. Verwendung nach Anspruch 4, wobei R₅ Wasserstoff, Alkyl mit 2 bis 22 Kohlenstoffatomen oder Alkylphenyl ist, dessen Alkylrest 4 bis 24 Kohlenstoffatome enthält.

6. Verwendung nach Anspruch 5, wobei R₁ Wasserstoff oder Hydroxy ist.

7. Verwendung nach Anspruch 6, wobei R₅ Wasserstoff, Alkyl mit 4 bis 12 Kohlenstoffatomen oder Alkylphenyl ist, dessen Alkylrest 4 bis 12 Kohlenstoffatome enthält.

8. Verwendung nach Anspruch 7, wobei einer der Reste R₃ und R₄ Niederalkyl mit 1 bis 3 Kohlenstoffatomen und der andere Wasserstoff ist.

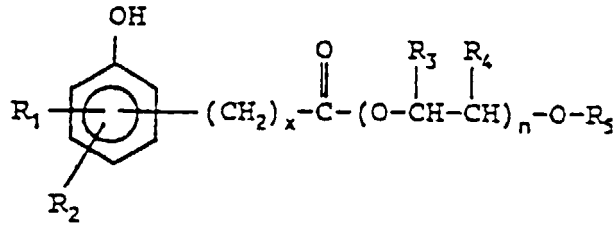
9. Verwendung nach Anspruch 8, wobei einer der Reste R₃ und R₄ Methyl oder Ethyl und der andere Wasserstoff ist.

10. Verwendung nach Anspruch 9, wobei x gleich 0, 1 oder 2 ist.

11. Verwendung nach Anspruch 10, wobei R₁ Wasserstoff ist, R₅ Alkylphenyl ist, dessen Alkylrest 4 bis 12 Kohlenstoffatome enthält, und x gleich 0 ist.

12. Verbindung der Formel:

5



10

oder ein kraftstofflösliches Salz davon; wobei

15

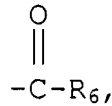
R₁ und R₂ jeweils unabhängig voneinander Wasserstoff, Hydroxy, Niederalkyl mit 1 bis 6 Kohlenstoffatomen oder Niederalkoxy mit 1 bis 6 Kohlenstoffatomen sind;

R₃ und R₄ jeweils Wasserstoff oder Ethyl sind, wobei einer der Reste R₃ und R₄ Ethyl und der andere Wasserstoff ist;

20

R₅ Wasserstoff, Phenyl, Aralkyl oder Alkaryl mit 7 bis 36 Kohlenstoffatomen oder ein Acylrest ist der Formel:

25



wobei R₆ Alkyl mit 1 bis 30 Kohlenstoffatomen, Phenyl oder Aralkyl oder Alkaryl mit 7 bis 36 Kohlenstoffatomen ist;

30

n eine ganze Zahl von 10 bis 50 ist; und x eine ganze Zahl von 0 bis 10 ist.

13. Verbindung nach Anspruch 12, wobei n eine ganze Zahl von 15 bis 30 ist.

35

14. Verbindung nach Anspruch 12, wobei R₁ Wasserstoff, Hydroxy oder Niederalkyl mit 1 bis 4 Kohlenstoffatomen ist; und R₂ Wasserstoff ist.

15. Verbindung nach Anspruch 14, wobei R₅ Wasserstoff oder Alkylphenyl ist, dessen Alkylrest 4 bis 24 Kohlenstoffatome enthält.

40

16. Verbindung nach Anspruch 15, wobei R₁ Wasserstoff oder Hydroxy ist.

17. Verbindung nach Anspruch 16, wobei R₅ Wasserstoff oder Alkylphenyl ist, dessen Alkylrest 4 bis 12 Kohlenstoffatome enthält

45

18. Verbindung nach Anspruch 17, wobei x gleich 0, 1 oder 2 ist.

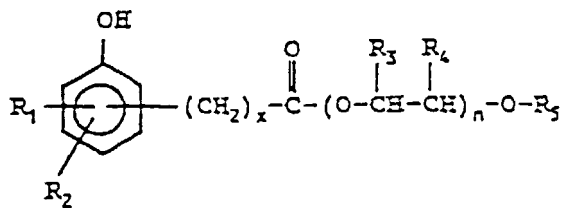
19. Verbindung nach Anspruch 18, wobei R₁ Wasserstoff ist, R₅ Alkylphenyl ist, dessen Alkylrest 4 bis 12 Kohlenstoffatome enthält, und x gleich 0 ist.

50

20. Kraftstoffzusammensetzung, umfassend eine größere Menge an Kohlenwasserstoffen des Benzin- oder Dieselsiebereichs und eine detergierend wirkende Menge einer Verbindung der Formel:

55

5



10

oder eines treibstofflöslichen Salzes davon; wobei

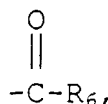
15

R₁ und R₂ jeweils unabhängig voneinander Wasserstoff, Hydroxy, Niederalkyl mit 1 bis 6 Kohlenstoffatomen oder Niederalkoxy mit 1 bis 6 Kohlenstoffatomen sind;

R₃ und R₄ jeweils unabhängig voneinander Wasserstoff oder Niederalkyl mit 1 bis 6 Kohlenstoffatomen sind;

20

R₅ Wasserstoff, Alkyl mit 1 bis 30 Kohlenstoffatomen, Phenyl, Aralkyl oder Alkaryl mit 7 bis 36 Kohlenstoffatomen oder ein Acylrest ist der Formel:



25

wobei R₆ Alkyl mit 1 bis 30 Kohlenstoffatomen, Phenyl oder Aralkyl oder Alkaryl mit 7 bis 36 Kohlenstoffatomen ist;

30

n eine ganze Zahl von 10 bis 50 ist; und x eine ganze Zahl von 0 bis 10 ist;

35

21. Kraftstoffzusammensetzung nach Anspruch 20, wobei R₁ Wasserstoff, Hydroxy oder Niederalkyl mit 1 bis 4 Kohlenstoffatomen ist; R₂ Wasserstoff ist; einer der Reste R₃ und R₄ Wasserstoff und der andere Methyl oder Ethyl ist; R₅ Wasserstoff, Alkyl mit 2 bis 22 Kohlenstoffatomen oder Alkylphenyl ist, dessen Alkylrest 4 bis 24 Kohlenstoffatome enthält, n gleich 15 bis 30 ist, und x gleich 0, 1 oder 2 ist.

40

22. Kraftstoffzusammensetzung nach Anspruch 21, wobei R₁ Wasserstoff oder Hydroxy ist; R₅ Wasserstoff, Alkyl mit 4 bis 12 Kohlenstoffatomen oder Alkylphenyl ist, dessen Alkylrest 4 bis 12 Kohlenstoffatome enthält; und x gleich 0 ist.

23. Kraftstoffzusammensetzung nach Anspruch 22, wobei R₁ Wasserstoff ist, und R₅ Alkylphenyl ist, dessen Alkylrest 4 bis 12 Kohlenstoffatome enthält.

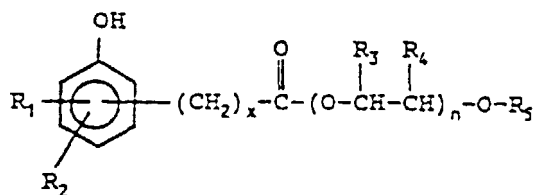
45

24. Kraftstoffzusammensetzung nach Anspruch 20, wobei die Zusammensetzung etwa 50 bis etwa 2500 Gewichtsteile pro Million der Verbindung enthält.

50

25. Kraftstoffkonzentrat, umfassend ein inertes stabiles oleophiles organisches Lösungsmittel, das im Bereich von etwa 66°C bis 200°C (150°F bis 400°F) siedet, und etwa 10 bis etwa 70 Gew.% einer Verbindung der Formel:

55

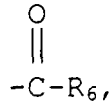


oder eines kraftstofflöslichen Salzes davon, wobei

R₁ und R₂ jeweils unabhängig voneinander Wasserstoff, Hydroxy, Niederalkyl mit 1 bis 6 Kohlenstoffatomen oder Niederalkoxy mit 1 bis 6 Kohlenstoffatomen sind;

R₃ und R₄ jeweils unabhängig voneinander Wasserstoff oder Niederalkyl mit 1 bis 6 Kohlenstoffatomen sind;

R₅ Wasserstoff, Alkyl mit 1 bis 30 Kohlenstoffatomen, Phenyl, Aralkyl oder Alkaryl mit 7 bis 36 Kohlenstoffatomen oder ein Acylrest ist der Formel:



wobei R₆ Alkyl mit 1 bis 30 Kohlenstoffatomen, Phenyl oder Aralkyl oder Alkaryl mit 7 bis 36 Kohlenstoffatomen ist;

n eine ganze Zahl von 10 bis 50 ist; und x eine ganze Zahl von 0 bis 10 ist.

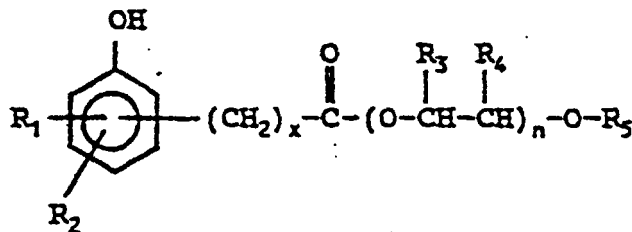
26. Kraftstoffkonzentrat nach Anspruch 25, wobei R₁ Wasserstoff, Hydroxy oder Niederalkyl mit 1 bis 4 Kohlenstoffatomen ist; R₂ Wasserstoff ist; einer der Reste R₃ und R₄ Wasserstoff und der andere Methyl oder Ethyl ist; R₅ Wasserstoff, Alkyl mit 2 bis 22 Kohlenstoffatomen oder Alkylphenyl ist, dessen Alkylrest 4 bis 24 Kohlenstoffatome enthält, n gleich 15 bis 30 ist, und x gleich 0, 1 oder 2 ist.

27. Kraftstoffkonzentrat nach Anspruch 26, wobei R₁ Wasserstoff oder Hydroxy ist; R₅ Wasserstoff, Alkyl mit 4 bis 12 Kohlenstoffatomen oder Alkylphenyl ist, dessen Alkylrest 4 bis 12 Kohlenstoffatome enthält; und x gleich 0 ist.

28. Kraftstoffkonzentrat nach Anspruch 27, wobei R₁ Wasserstoff ist, und R₅ Alkylphenyl ist, dessen Alkylrest 4 bis 12 Kohlenstoffatome enthält.

Revendications

1. Utilisation d'un composé de formule :

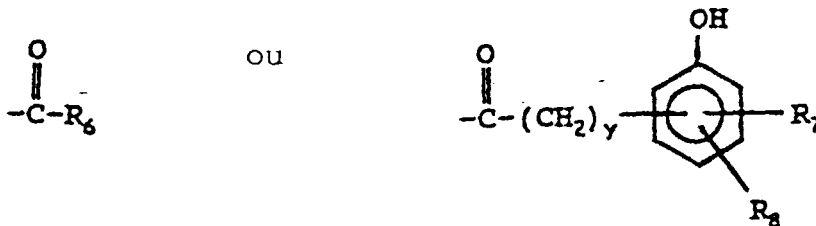


ou d'un de ses sels solubles dans les carburants ; formule dans laquelle

R₁ et R₂ représentent chacun indépendamment l'hydrogène, un groupe hydroxy, alkyle inférieur ayant 1 à 6 atomes de carbone ou alkoxy inférieur ayant 1 à 6 atomes de carbone ;

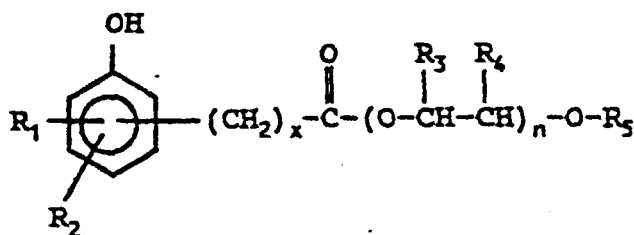
R₃ et R₄ représentent chacun indépendamment l'hydrogène ou un groupe alkyle inférieur ayant 1 à 6 atomes de carbone ;

R₅ représente l'hydrogène, un groupe alkyle ayant 1 à 30 atomes de carbone, phényle, aralkyle ou alkaryl ayant 7 à 36 atomes de carbone, ou un groupe acyle répondant à la formule :



15 dans laquelle R_6 représente un groupe alkyle ayant 1 à 30 atomes de carbone, phényle, ou aralkyle ou alkaryle ayant 7 à 36 atomes de carbone ; R_7 et R_8 représentent chacun indépendamment l'hydrogène, un groupe hydroxy, alkyle inférieur ayant 1 à 6 atomes de carbone ou alkoxy inférieur ayant 1 à 6 atomes de carbone ; n représente un nombre entier de 5 à 100 ; et x et y représentent chacun indépendamment un nombre entier de 0 à 10 ; comme additif dans une composition de carburant comprenant une quantité dominante d'hydrocarbures bouillant dans la plage de l'essence ou du carburant diesel, pour limiter les dépôts dans les moteurs.

- 20
2. Utilisation suivant la revendication 1, dans laquelle n représente un nombre entier de 10 à 50.
- 25
3. Utilisation suivant la revendication 2, dans laquelle n représente un nombre entier de 15 à 30.
- 30
4. Utilisation suivant la revendication 2, dans laquelle R_1 représente l'hydrogène, un groupe hydroxy ou alkyle inférieur ayant 1 à 4 atomes de carbone, et R_2 représente l'hydrogène.
- 35
5. Utilisation suivant la revendication 4, dans laquelle R_5 représente l'hydrogène, un groupe alkyle ayant 2 à 22 atomes de carbone ou alkyphényle ayant un groupe alkyle contenant 4 à 24 atomes de carbone.
- 40
6. Utilisation suivant la revendication 5, dans laquelle R_1 représente l'hydrogène ou un groupe hydroxy.
- 45
7. Utilisation suivant la revendication 6, dans laquelle R_5 représente l'hydrogène, un groupe alkyle ayant 4 à 12 atomes de carbone ou alkyphényle ayant un groupe alkyle contenant 4 à 12 atomes de carbone.
- 50
8. Utilisation suivant la revendication 7, dans laquelle un des groupes R_3 et R_4 représente un groupe alkyle inférieur ayant 1 à 3 atomes de carbone et l'autre représente l'hydrogène.
- 55
9. Utilisation suivant la revendication 8, dans laquelle un des groupes R_3 et R_4 représente un groupe méthyle ou éthyle et l'autre représente l'hydrogène.
10. Utilisation suivant la revendication 9, dans laquelle x est égal à 0, 1 ou 2.
11. Utilisation suivant la revendication 10, dans laquelle R_1 représente l'hydrogène, R_5 représente un groupe alkyphényle ayant un groupe alkyle contenant 4 à 12 atomes de carbone et x est égal à 0.
12. Composé de formule :

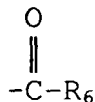


ou d'un de ses sels solubles dans les carburants ; formule dans laquelle

R₁ et R₂ représentent chacun indépendamment l'hydrogène, un groupe hydroxy, alkyle inférieur ayant 1 à 6 atomes de carbone ou alkoxy inférieur ayant 1 à 6 atomes de carbone ;

R₃ et R₄ représentent chacun l'hydrogène ou un groupe éthyle, un des groupes R₃ et R₄ représentant un groupe éthyle et l'autre représentant l'hydrogène ;

R₅ représente l'hydrogène, un groupe phényle, aralkyle ou alkaryle ayant 7 à 36 atomes de carbone, ou un groupe acyle répondant à la formule :



dans laquelle R₆ représente un groupe alkyle ayant 1 à 30 atomes de carbone, phényle, ou aralkyle ou alkaryle ayant 7 à 36 atomes de carbone ;

n représente un nombre entier de 10 à 50 ; et x représente un nombre entier de 0 à 10.

13. Composé suivant la revendication 12, dans lequel n représente un nombre entier de 15 à 30.

14. Composé suivant la revendication 12, dans lequel R₁ représente l'hydrogène, un groupe hydroxy ou alkyle inférieur ayant 1 à 4 atomes de carbone, et R₂ représente l'hydrogène.

15. Composé suivant la revendication 14, dans lequel R₅ représente l'hydrogène ou un groupe alkylphényle ayant un groupe alkyle contenant 4 à 24 atomes de carbone.

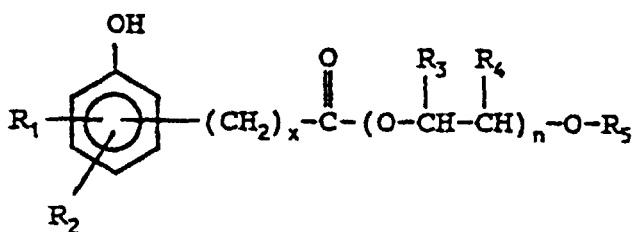
16. Composé suivant la revendication 15, dans lequel R₁ représente l'hydrogène ou un groupe hydroxy.

17. Composé suivant la revendication 16, dans lequel R₅ représente l'hydrogène ou un groupe alkylphényle ayant un groupe alkyle contenant 4 à 12 atomes de carbone.

18. Composé suivant la revendication 17, dans lequel x est égal à 0, 1 ou 2.

19. Composé suivant la revendication 18, dans lequel R₁ représente l'hydrogène, R₅ représente un groupe alkylphényle ayant un groupe alkyle contenant 4 à 12 atomes de carbone et x est égal à 0.

20. Composition de carburant comprenant une quantité dominante d'hydrocarbures bouillant dans la plage de l'essence ou du carburant diesel et une quantité détergente efficace d'un composé de formule :

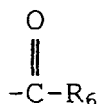


ou d'un de ses sels solubles dans les carburants ; formule dans laquelle

R₁ et R₂ représentent chacun indépendamment l'hydrogène, un groupe hydroxy, alkyle inférieur ayant 1 à 6 atomes de carbone ou alkoxy inférieur ayant 1 à 6 atomes de carbone ;

R₃ et R₄ représentent chacun indépendamment l'hydrogène ou un groupe alkyle inférieur ayant 1 à 6 atomes de carbone ;

R₅ représente l'hydrogène, un groupe alkyle ayant 1 à 30 atomes de carbone, phényle, aralkyle ou alkaryle ayant 7 à 36 atomes de carbone, ou un groupe acyle de formule :



5

dans laquelle R_6 représente un groupe alkyle ayant 1 à 30 atomes de carbone, phényle, ou aralkyle ou alkaryle ayant 7 à 36 atomes de carbone ;

n représente un nombre entier de 10 à 50 ; et x représente un nombre entier de 0 à 10.

10

21. Composition de carburant suivant la revendication 20, dans laquelle R_1 représente l'hydrogène, un groupe hydroxy ou alkyle inférieur ayant 1 à 4 atomes de carbone ; R_2 représente l'hydrogène ; un des groupes R_3 et R_4 représente l'hydrogène et l'autre représente un groupe méthyle ou éthyle ; R_5 représente l'hydrogène, un groupe alkyle ayant 2 à 22 atomes de carbone ou alkylphényle ayant un groupe alkyle contenant 4 à 24 atomes de carbone ; n a une valeur de 15 à 30 et x est égal à 0, 1 ou 2.

15

22. Composition de carburant suivant la revendication 21, dans laquelle R_1 représente l'hydrogène ou un groupe hydroxy ; R_5 représente l'hydrogène, un groupe alkyle ayant 4 à 12 atomes de carbone ou alkylphényle ayant un groupe alkyle contenant 4 à 12 atomes de carbone ; et x est égal à 0.

20

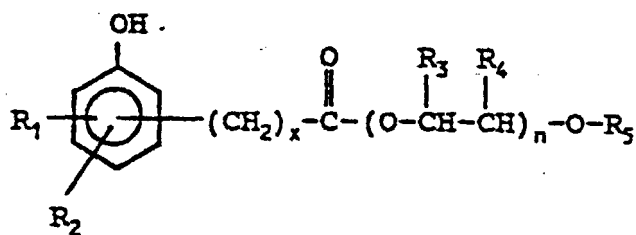
23. Composition de carburant suivant la revendication 22, dans laquelle R_1 représente l'hydrogène et R_5 représente un groupe alkylphényle ayant un groupe alkyle contenant 4 à 12 atomes de carbone.

24. Composition de carburant suivant la revendication 20, qui contient environ 50 à environ 2500 parties par million en poids dudit composé.

25

25. Concentré pour carburant, comprenant un solvant organique oléophile stable inerte bouillant dans la plage d'environ 66°C à 200°C (150°F à 400°F) et environ 10 à environ 70 pour cent en poids d'un composé de formule :

30



35

ou d'un de ses sels solubles dans les carburants ; formule dans laquelle

40

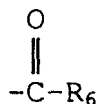
R_1 et R_2 représentent chacun indépendamment l'hydrogène, un groupe hydroxy, alkyle inférieur ayant 1 à 6 atomes de carbone ou alkoxy inférieur ayant 1 à 6 atomes de carbone ;

R_3 et R_4 représentent chacun indépendamment l'hydrogène ou un groupe alkyle inférieur ayant 1 à 6 atomes de carbone ;

45

R_5 représente l'hydrogène, un groupe alkyle ayant 1 à 30 atomes de carbone, phényle, aralkyle ou alkaryle ayant 7 à 36 atomes de carbone, ou un groupe acyle de formule :

50



dans laquelle R_6 représente un groupe alkyle ayant 1 à 30 atomes de carbone, phényle, ou aralkyle ou alkaryle ayant 7 à 36 atomes de carbone ;

55

n représente un nombre entier de 10 à 50 ; et x représente un nombre entier de 0 à 10.

26. Concentré pour carburant suivant la revendication 25, dans lequel R_1 représente l'hydrogène, un groupe hydroxy

EP 0 636 164 B1

ou alkyle inférieur ayant 1 à 4 atomes de carbone ; R_2 représente l'hydrogène ; un des groupes R_3 et R_4 représente l'hydrogène et l'autre représente un groupe méthyle ou éthyle ; R_5 représente l'hydrogène, un groupe alkyle ayant 2 à 22 atomes de carbone ou alkylphényle ayant un groupe alkyle contenant 4 à 24 atomes de carbone ; n a une valeur de 15 à 30 et x est égal à 0, 1 ou 2.

5

27. Concentré pour carburant suivant la revendication 26, dans lequel R_1 représente l'hydrogène ou un groupe hydroxy ; R_5 représente l'hydrogène, un groupe alkyle ayant 4 à 12 atomes de carbone ou alkylphényle ayant un groupe alkyle contenant 4 à 12 atomes de carbone ; et x est égal à 0.

10

28. Concentré pour carburant suivant la revendication 27, dans lequel R_1 représente l'hydrogène et R_5 représente un groupe alkylphényle ayant un groupe alkyle contenant 4 à 12 atomes de carbone.

15

20

25

30

35

40

45

50

55